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Article

Nutrients Load Estimation in a Regulated Streamflow Estuary: The São Francisco Estuary (NE/Brazil)

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Abstract

This study aimed to estimate the nutrients concentration variability in the São Francisco estuary from observed data during the summer and winter seasons of 2014 and to assess the influence of outflow discharges, circulation and precipitation on nutrients fluxes exchange. The marginal difference in the streamflow (1,160 m^3/s - summer; 1,260 m^3/s - winter) reflected the small role of the river discharge on the variability of the nutrients load. The increase in the sediments load from February (13189.70 T/month) to July (36088.56 T/month) revealed that high precipitation (153.6 mm - winter; 37.6 mm - summer) and internal circulation might have contributed to enhancing the sediment budge towards the estuary mouth. The strong current velocity in July (~0.9 m/s) revealed more potential to export estuarine waters towards the coast when compared to ~0.7 m/s (February). The concentrations and nutrients load were higher during the winter season led by phosphate (3.70 μgL^{-1}) and NID (83.64 $\mu g\ L^{-1}$), against (1.38 μgL^{-1} and 30.70 μgL^{-1} - summer), except for silicates with 4.20 mgL^{-1} (summer) and 3.59 mgL^{-1} (winter). Despite the active control of outflows, the internal circulation, followed by local precipitation, are considered the main mechanisms behind the increased nutrients load within the estuary.

Keywords: river discharge, nutrients load, São Francisco estuary.

Estimativa da Carga de Nutrientes em um Estuário com Vazão Controlada: O Estuário do Rio São Francisco (NE/Brasil)

Resumo

Este estudo teve como objetivo estimar a variabilidade da concentração de nutrientes no estuário do São Francisco a partir de dados observados durante o verão e o inverno de 2014, e avaliar a influência da vazão, circulação e precipitação no balanço dos fluxos de nutrientes. A diferença marginal nas vazões (1.160 m^3/s - verão; 1.260 m^3/s - inverno) refletiu o pequeno papel da descarga do rio na variabilidade da carga de nutrientes. O aumento da carga de sedimentos de fevereiro (13189,70 T/mês) a julho (36088,56 T/mês) revelou que a alta precipitação (153,6 mm - inverno; 37,6 mm - verão) e a circulação interna podem ter contribuído para aumentar a carga de sedimentos em direção à foz do estuário. A forte velocidade da corrente em julho (~ 0,9 m/s) revelou um maior potencial para exportar águas estuarinas em direção à costa quando comparada à ~ 0,7 m/s (fevereiro). As concentrações e carga de nutrientes foram maiores durante o inverno, liderado pelo fosfato (3,70 μgL^{-1}) e NID (83,64 μgL^{-1}), seguida por (1,38 μgL^{-1} e 30,70 μgL^{-1} - verão), com exceção para silicatos com 4,20 mgL^{-1} (verão) e 3,59 mgL^{-1} (inverno). Apesar do controle ativo das vazões, a circulação interna, seguida pela precipitação local, foram consideradas os principais mecanismo responsáveis pelo aumento da carga de nutrientes no estuário.

Palavras-chave: vazão do rio, carga de nutrientes, estuário do São Francisco.

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1. Introduction

The fluvial transport of matter from the continents to the oceans through the continental drainage is a fundamental process for the planet's structural and functional formation and the continent-ocean geology and biochemistry interface (Liu *et al.*, 2010). Numerous characteristics of the hydrological contribution of river flow are associated with the transport of matter, such as the total suspended solids and nutrients, and their final dispersion as coastal plumes on the continental shelf (Knoppers *et al.*, 2018; Oliveira *et al.*, 2012). Therefore, the dispersed matters are subject to significant changes in their physical, chemical and biological characteristics, due to drastic modifications in the hydrological regime caused by anthropogenic changes related to economic activities, hydroelectric dams, reservoirs, land use and irrigation channels (Souza and Knoppers, 2003; Salomoni *et al.*, 2007).

The São Francisco River (RSF) basin, with 640,000 km^2 has along its course a system of seven cascading dams controlling 98% of the drainage basin, which considerably altered the hydrological regime mainly in the middle-low sector of the basin, modifying water discharges, the load of suspended matter and nutrients (Knoppers *et al.*, 2006; Medeiros *et al.*, 2011a, Knoppers *et al*., 2018). Since several years of implementation of the dams in the SFR basin, a substantial number of studies have been reported on the impact of flow regularization in the lower stretch of the SFR on the water physical-chemical characteristics (Souza and Knoppers, 2003; Marques *et al.*, 2004; Knoppers *et al.*, 2006; Milliman *et al.*, 2008), nutrient loads (Sabadini - Santos *et al.*, 2009; 2013; Melo - Magalhães *et al.*, 2011; Oliveira *et al.*, 2012; Medeiros *et al.*, 2007; 2015; 2018; Holanda *et al.*, 2017), and saline wedge migration (Cavalcante *et al*., 2017; 2020).

Apart from the severe coastal erosion, loss of seasonal inundation and the decline of fisheries due to the oligotrophic waters, perhaps the most important impact induced by the diminished and more constant river flow is the severe reduction of the material concentrations and nutrient loads in SFR estuary (Knoppers *et al.*, 2006; Medeiros *et al*., 2007). Nutrient loadings are regarded as a key environmental player for monitoring the changes on the drainage basin and its effects on the estuary ecological dynamics on a regional, as well as global scale (Nowlin *et al.*, 2005). In that sense, much effort has been made for accurate detection, identification and estimation of nutrients fluxes in rivers and estuarine waters (Nowlin *et al.*, 2005).As indicated previously, although several studies have been conducted in the SFR estuary after the implementation of the last dam in late 1994 (Xingó dam), the majority of the studies were based on data before 2012, prior to the streamflow reduction caused by the extreme drought event initiated in late 2012 (Cavalcante *et al.*, 2020).

To our knowledge, there are only a paucity of studies conducted in the SF estuary encompassing the extreme drought period but mainly focusing on the estuarine circulation and salt dynamics between the estuary and its coastal zone (Cavalcante *et al.*, 2017; Cavalcante *et al.*, 2020; Fonseca *et al.*, 2020; Paiva *et al.*, 2020). Considering the economic and social importance of the estuary for the local population, and the direct role played by the nutrients on the ecological equilibrium of the system, there are no previous studies evaluating the nutrients loadings variability under the new streamflow regime initiated in late 2012. Therefore, our objective is to estimate the nutrients concentrations variability in the SFR estuary from observed data during the summer and winter seasons of 2014 and to assess the influence of outflow discharges, circulation and precipitation on nutrients fluxes exchange.

2. Study Area

The São Francisco River Basin (RSF) has along its course a system of seven cascading dams where the hydroelectric power stations were installed (Knoppers *et al*., 2006) as indicated in Table 1.

The fluvial-marine deltaic plains of the Lower SFR started at Penedo city in Alagoas States and reaches the litoral zone including pleistocene marine terraces and intersected by freshwater wetlands, beach-ridges, sand dunes and beaches (Dominguez, 1996). Figure 1 show the SFR estuary.

According to Knoppers *et al.* (2006) the basin traverses several climatic regimes and comprises several physiographic compartments. It is traditionally divided into the Upper, Middle, SubMiddle and Lower SFR sector. The climate varies from tropical humid (i.e. Upper SFR and Lower SFR) to semiarid (i.e. Sub-Middle SFR). In the SFR estuary the climate is tropical humid with raining season in the winter months (Medeiros *et al.*, 2011a).

Table 1 - Hidroelectric power stations along the São Francisco river.

Hidroelectric Station	Volume (hm^3)	Physiographic regions
UHE Três Marias	19,528.00	Upper São Francisco
UHE Sobradinho	34,117.00	Sub - Middle São Francisco
UHE Luiz Gonzaga (Itaparica)	10,782.00	Sub - Middle São Francisco
UHE Apolônio Sales (Antiga Moxotó)	1,277.00	Lower São Francisco
UHE Paulo Afonso I/III	26.00	Lower São Francisco
UHE Paulo Afonso IV	1,277.00	Lower São Francisco
UHE Xingó	3,800.00	Lower São Francisco

Source: Agência Nacional de Aguas (ANA, 2020).

3. Material and Methods

A total of two field campains were performed in 2014. The surveys were conducted in summer - dry season (18-19 February), and winter - rain season (16-17 July) during spring tide (Fig. 1). The location of the stations were based on previous studies in the study area (Medeiros *et al.*, 2015). The measurements were combined with transects along-channel (depth 5-10 m) around high slack water (P1-P9) and at the anchor station (EF0 - 11 m depth) over two tidal cycles (Fig. 1). The physical-chemical parameters (salinity, pH, chlorophyll and turbidity) were obtained *in situ* with a YSI 6600 multi-parameter probe. The water samples for nutrient analysis were collected from the subsurface (≅ 0.4 m), using a Van Dorn-type bottle, and stored in polyethylene bottles and preserved on ice until laboratory processing. The samples were analyzed for dissolved inorganic nutrients (ammonium, nitrate, nitrite, phosphate and silica) according to Grasshoff *et al.* (1999). The chlorophyll-a and total suspended solids were analyzed according to Strickland and Parsons (1972). At the anchor station (EF0) the vertical profiles from surface to near bottom were performed at 30 min intervals over 25-h. A SonTek 1.5 MHz (ADP) was used to measure current speed and direction at a vertical resolution of 0.5 m during 25-h, and the YSI probe for the physical-chemical parameters. The estimative of the dissolved inorganic nutrient fluxes followed the description in Medeiros *et al.* (2007) and is indacted in the Eq. (1). Water discharges were obtained at Traipu-AL station provided by ANA.

$$F_m = Q \times C_i \qquad (1)$$

where F_m is the momentary nutrient flux, Q is the outflow in m^3/s and C_i is the mean concentration of nutrients.

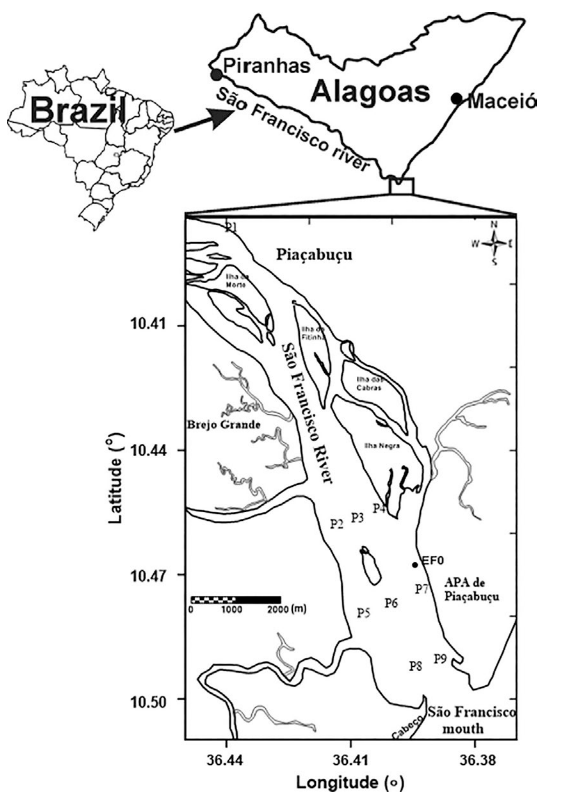

Figure 1 - Study area in lower São Francisco River showing the spation distribution of the sampling stations (EF0, P1- P9), and anchor station (EF0). (Coordinates: 10.38-10.51° N and 36.44-36.38° W). The section area varies between 1.5 km (P2-P4) and 2 km (P5-P7).

4. Results and Discussion

4.1. River discharge, precipitation and tide height

The streamflow indicated a small change on flow rate between the two measurement periods in February and July 2014 (Fig. 2A). The discharged varied from approximately 1,160 m^3/s in February to about 1,260 m^3/s in July. Although the year 2014 was already under influence of the drought event that started in late 2012, the streamflow released at the Xingó's dam was within the minimum rate of 1,100-1,300 m^3/s traditionally set by the ANA (ONS, 2018) to avoid ecological problems, which was reflected in the small role of the river discharge on the temporal variability of the nutrients load found in the SFR estuary.

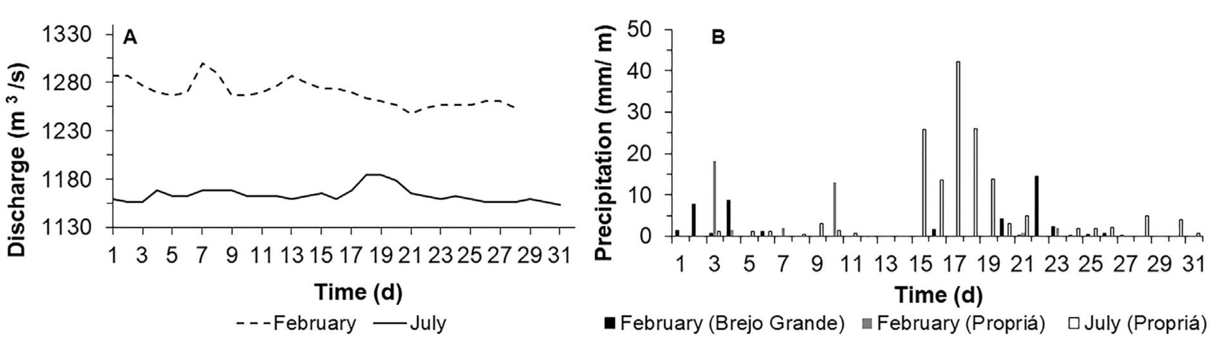

Figure 2 - River discharge for February and July 2014 at Traipu-AL station from ANA (A), and daily precipitation rate at Brejo Grande and Propriá-SE sations from INMET (B).

The Brejo Grande station (10 km northwest of the sampling stations) recorded an accumulated rainfall of 43.8 mm in February (Fig. 2B). At the conventional station in Propriá, a cumulative rainfall of 37.6 mm was recorded in February and increased to 153.6 mm in July 2014, which suggested a more active role in the availability and nutrients load for the study period. According to Medeiros *et al.* (2011b; 2018) precipitations located in the lower sector of the SFR basin are more efficient in producing matters to be transported by the river than intense precipitations rates in the upper sectors of the basin.

The tide elevation obtained from the Brazilian Tide Charts ranged from 1.7 m to 1.85 m on 18-19 February and 16-17 July 2014, respectively. These results were aspected as both measurements were conducted during the spring tide.

4.2. Environmental variables

The São Francisco estuary is mainly controlled by the fluvial discharge and tidal oscillations, and according to the vertical stratification of salinity, it is classified as partially mixed with high stratification (Cavalcante *et al.*, 2017). The surface to bottom along-channel current velocity observed at the anchor station (EF0) indicated a strong asymmetry between the ebb and flood currents for both February and July months (Fig. 3A,C). Maximum values of currents at about 0.7 m/s and 0.9 m/s were found near the surface layer during the peak ebb flow phase at about low tide period in February and July, respectively (Fig. 3A,C). Overall, the ebb and flood currents were stronger in July 2014, which are in agreement with values observed in the spring tide in the Caravelas estuary - Bahia state (Schettini and Miranda, 2010). It was found a delay of about two hours between the tide-slack period and the inversion from ebb to flood current direction in both months. Such pattern was attributed to the time that the river took to export the water that entered the estuary during the flood tide.

The superficial salinity over the 25 h period of the measurements, reached values above 30 g/kg at 2 meters of depth in both months (Fig. 3 B, D). The vertical salinity gradient in 2014 revealed a highly stratified water column in agreement with what was verified by Cavalcante *et al.* (2017), and can be associated with the downstream flow towards the estuary mouth (Medeiros *et al.*, 2014). On the other hand, in the years 2006 and 2007, it was found an increase in salinity levels in the estuary inner areas revealing a more well-mixed water due to the intrusion of seawater as a result of the streamflow at ~1000 m^3/s (Melo-Magalhães *et al.*, 2011).

The overall temperature varied from 28.8 °C to 26.0 °C with an amplitude of 1.7 °C and 1.3 °C, in February and July, respectively. The slight cooler waters in July may be related to the rainy season as well as associated with the transport of colder ocean water towards the SFR mouth by the SE wind (Cavalcante *et al.*, 2020). Similar results were found by Cavalcante *et al.* (2017), where values between 27.8 °C and 29.6 °C were observed in February 2014. Medeiros *et al.* (2016), observed values that varied from 26.8 °C to 27.9 °C, for the years 2001, 2004 and 2007, where the hydrological conditions changed from drought to rain enhacing water availabity compared with normal conditions.

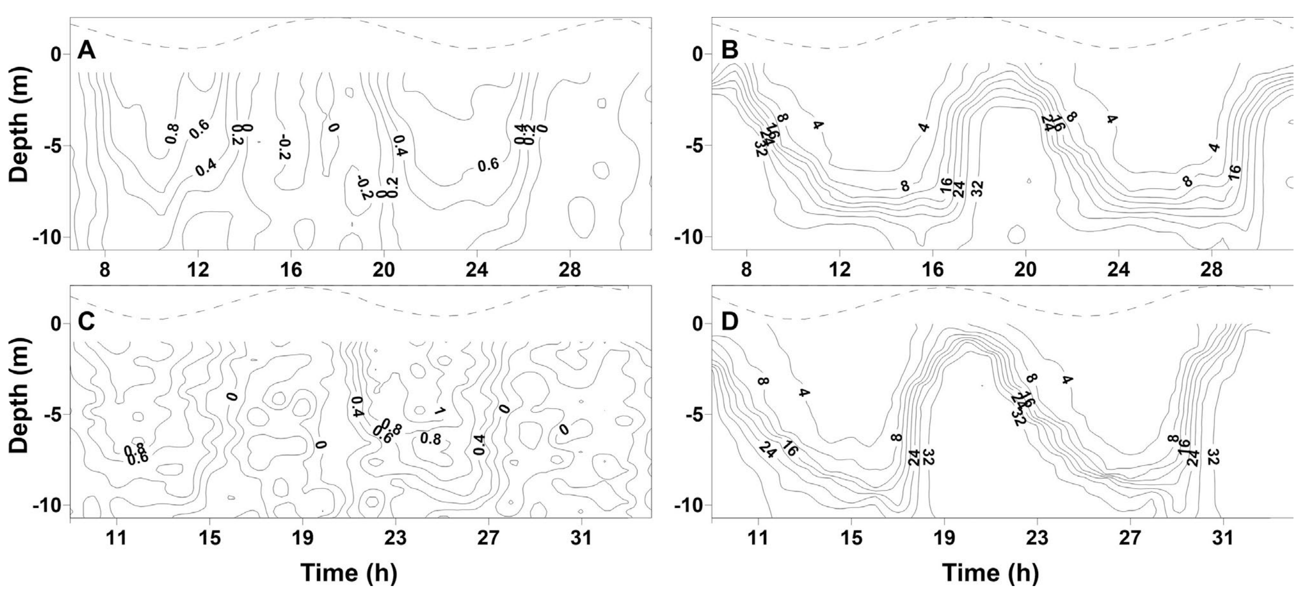

Figure 3 - Temporal and vertical variation of the along-channel current speed and salinity during two tidal cycles between 18-19 February (A,B) and 16-17 July (C,D). Positive current velocity means downstream and negative means upstream.

4.3. Inorganic nutrients

The dissolved inorganic nutrients (DIN) showed the lowest concentrations for the São Francisco River estuary when compared to previous studies by Santos (1993) and Medeiros *et al.* (2011b; 2016). Table 2 shows all variables analyzed based on sampling at the anchor station (EF0) and along the estuary main channel (P1 to P9).

The pH varied between 7.45 and 8.17 (average: 7.71) in the dry season (February), and from 7.10 to 8.29 (average: 7.61) in the rainy season (July). The slight increase in the maximum range of pH in July might be associated with the input of hydroxides transported downstream as a result of intense precipitation observed in July 2014 (Medeiros *et al.*, 2016; 2018). Indeed, according to Medeiros *et al.* (2016), during years with high precipitation rates intense bottom leaching occurs in the SFR basin, removing hydroxides from the rocks which in turn will increase the pH levels towards the estuary region.

The spatial distribution of chlorophyll-a (Cl-a) showed a slight increase during the rainy period (July), reaching a maximum of 6.5 µg/L against the 1.4 µg/L in February (dry period). It was found a difference of ≈ 1.2 µg/L in the Cl-a average values which varied between 1.1 µg/L (February) and 2.4 µg/L (July) (Table 2). These findinds might be associated with the high levels of nutrients observed in July, and corroborate the results reported by Lima and Severi (2014) and Medeiros *et al.* (2016) for the SF estuary.

Table 2 - Statistical analysis of sampled and estimated variables collected at the anchor station (EF0) and along the estuary main channel in February and July of 2014.

		Anchor station					Spatial stations				
Months	Variables	Max	Min	$\bar{x}$	σ	cv	Max	Min	$\bar{x}$	σ	cv
February	Salinity (g/kg)	25.88	0.33	4.21	4.31	1.02	4.65	0.01	2.12	1.39	0.65
	Temperature (°C)	29.33	27.75	28.81	0.36	0.01	28.64	27.67	28.29	0.35	0.01
	pH (íons gL^{-1})	8.17	7.45	7.71	0.18	0.02	7.90	7.63	7.73	0.08	0.01
	Turbidity (NTU)	4.90	2.70	3.57	0.51	0.14	4.80	2.70	3.31	0.65	0.20
	TSS (mgL^{-1})	10.93	1.80	4.32	2.03	0.47	7.60	1.77	3.80	1.75	0.46
	Cl-a (μgL^{-1})	1.79	0.13	1.03	0.42	0.40	1.44	0.77	1.16	0.24	0.21
	Si-SiO_2 (mgL^{-1})	4.99	2.67	4.20	0.69	0.16	4.61	2.97	3.83	0.53	0.14
	P-PO_4^{-3} (μgL^{-1})	7.99	0.31	1.38	1.69	1.22	1.30	0.31	0.64	0.49	0.77
	P- HPO_4^{-2} (μgL^{-1})	55.80	4.22	13.29	10.15	0.76	13.96	7.47	9.99	1.83	0.18
	N-NH_4 (μgL^{-1})	29.40	0.14	13.48	8.69	0.64	33.60	4.22	12.02	9.55	0.79
	N-NO_2 (μgL^{-1})	0.57	0.14	0.19	0.12	0.65	0.29	0.14	0.19	0.07	0.39
	N-NO_3 (μgL^{-1})	153.99	0.14	17.03	30.80	1.81	3.92	0.14	1.82	1.48	0.81
	DIN (μgL^{-1})	168.05	1.12	30.70	30.92	1.01	36.96	5.88	14.03	9.98	0.71
	N:P	167.60	3.62	45.65	45.41	0.99	119.23	9.74	31.95	33.76	1.06
July	Salinity (g/kg)	29.39	0.42	4.92	6.26	1.27	6.56	0.79	3.46	1.82	0.52
	Temperature (°C)	26.24	25.28	25.85	0.24	0.01	26.33	25.79	26.05	0.17	0.01
	pH (íons gL^{-1})	8.29	7.10	7.61	0.30	0.04	7.95	7.68	7.80	0.10	0.01
	Turbidity (NTU)	13.70	3.60	5.32	2.09	0.39	8.00	4.30	5.24	1.10	0.21
	TSS (mgL^{-1})	57.00	4.75	11.57	10.71	0.93	13.25	6.50	9.18	2.53	0.28
	Cl-a (μgL^{-1})	2.35	0.38	1.51	0.51	0.34	6.49	1.20	2.35	1.67	0.71
	Si-SiO_2 (mgL^{-1})	4.37	3.00	3.59	0.38	0.11	4.15	3.66	3.90	0.17	0.04
	P-PO_4^{-3} (μgL^{-1})	7.79	1.30	3.70	1.63	0.44	6.17	2.92	4.36	0.98	0.22
	P- HPO_4^{-2} (μgL^{-1})	33.43	7.47	14.72	6.19	0.42	17.20	9.09	12.52	2.62	0.21
	N-NH_4 (μgL^{-1})	55.66	5.06	17.38	11.76	0.68	21.00	4.22	9.35	4.90	0.52
	N-NO_2 (μgL^{-1})	2.00	2.00	2.00	0.00	0.00	2.00	2.00	2.00	0.00	0.00
	N-NO_3 (µgL-1)	87.60	36.64	64.26	14.47	0.23	75.28	59.04	67.88	5.63	0.08
	DIN (μgL^{-1})	110.60	53.82	83.64	13.79	0.16	97.72	65.26	79.22	9.11	0.11
	N:P	78.24	8.64	29.60	19.45	0.66	26.26	12.76	18.97	4.60	0.24

$\bar{x}$: average; σ: standard deviations and cv: coefficient of variation.

In the work performed by Knoppers *et al.* (2006) it was indicated that low productivity in the SFR estuary was attributed to low concentrations of DIN and PO_4^{-3}. Our results indicated that among the forms of dissolved inorganic nitrogen, the nitrate was the most abundant followed by ammonium with both showing higher concentrations along the spatial stations in February and July (Table 2). This can be an indication of entry of this constituent by the rivers, precipitation or even by local surface washing Knoppers *et al.* (2006). The lowest concentrations were found for nitrite and may be related to the various processes that occur for the transformation of nitrogen in reservoirs. According to Esteves (1998), the nitrite is a nutrient rapidly consumed in the nitrification and denitrification processes, as well as during the ammonia oxidation which may explain the nitrite low concentrations.

At the EF0 station, nitrate contributed approximately 76% of the NID (ammonium + nitrite + nitrate) in July 2014, in agreement with the range reported by Borges (2014) for the Paraíba do Sul River delta (50 to 85%). In February, the nitrate contributed 55.5 % followed by ammonium ion with 43.9% of the total NID. Conversely, along the spatial stations the nitrate and nitrite were found at the lowest levels in February 2014, which can be attributed to the reduced water content due to the low precipitation rates in the region. The concentrations in nitrogenous forms throughout the spatial stations revealed higher concentrations depending on the location of the station when comparing with the anchor station (EF0). According to Borges (2014), the nutrient concentrations (PID and NID) in the Paraíba do Sul estuary decreased when the river reached the mouth of the system (salt ± 30), which are in agreement with out findings. The author attributed such reduction by the mixing of the waters into the coastal plume and by dispersing through advective processes generated by coastal currents.

The N:P ratio (16:1) of Redfield (1958) describes the elemental composition and the ideal demand for phytoplankton productivity. In our study, the N:P showed low values in July which was attributed to the increase in the concentration of NID in relation to PO_4^{-3}. The phosphate (PO_4^{-3}) at the EF0 station contributed ~11% of its total form (HPO_4^{-2}) in the dry period (February) and increased to ~25% of its total form during the rainy period (July). Again, the low values of PO4 in February might be attributed to the reduced precipitation rate and the exchange of estuarine water during flood tide, allowing its consumption by the phytoplankton in the water column, in agreement with previous studies (Knoppers *et al.*, 2006; Medeiros *et al.*, 2016).

On the other hand, the total phosphorus found in our study were lower than reported in Medeiros *et al.* (2011b). Dissolved inorganic phosphorus in shallow estuarine and coastal waters is rapidly transformed by biogeochemical processes ranging from adsorption-desorption or sorption to particles and biological assimilation Deborde *et al.* (2007). The SF estuary is a shallow water body which facilitates such biogeochemical transformations considering these processes are normally triggered when salinity ranging from 0-5 g/kg as verified by Deborde *et al.* (2007) in the Gironde estuary in France, and Borges (2014) in the estuarine delta of the Paraíba do Sul River in Brazil. Indeed, our NID rates towards the estuary mouth, confirmed a similar pattern in both periods (February and July 2014).

Silicate is the inorganic nutrient with the highest concentrations in the SF estuary. This nutrient is used by the microalgae of the group of diatoms and silicoflagellates to form their frustules (Reviers, 2006), and is considered as non-limiting in lake ecosystems due to its abundance in soils (Esteves, 1998). The higher concentration of this nutrient in February (4.2 mg/L), in contrast to 3.6 mg/L in July 2014, may be associated with less removal or consumption of silica by microalgae (Darley, 1982). The slightly lower concentration of silicates in the rainy season (July) can be attributed to the strong water exchange (0.9 m/s) and elevated tidal range (1.85 m), which would play a role in enhancing the dilution process in the marine waters (Cavalcante *et al.*, 2017; 2020). In our study, the concentration of silicates throughout the spatial stations (P1-P9) remained constant in both sampling periods in February and July 2014, in agreement with values reported in previous studies in the SF estuary (Medeiros *et al.*, 2011b; 2016).

The results for total suspended sediment (TSS) and turbidity at EF0 station indicated higher concentrations in the rainy season (July) with 11.57 mg/L and 5.32 NTU, against 4.32 mg/L and 3.57 NTU in the dry season (February), respectively, despite the slight decrease in streamflow in the early period. Such findings can be attributed to the low material availability in the lower stretch of the SF river channel caused by the sediment retention by the dams in the middle-sector of the SFR basin, and the capacity loss of the river to transport material towards the estuary region due to streamflow reduction (Knoppers *et al.*, 2006; Medeiros *et al.*, 2007; 2014). In that sense, local precipitation combined with the estuarine internal circulation would be the major forcings acting in the remobilization of the sediment in suspension originated by the erosion of the margins at local scale (Medeiros *et al.*, 2014; Cavalcante *et al.*, 2017; Melo - Magalhães *et al.*, 2011). Another explanation for the high TSS and turbidity levels in July is that as the surveys were performed during spring tide, the greater tidal amplitude would generate strong internal turbulence causing more resuspension of sediments in the water column.

4.4. Nutrient fluxes

The nutrients load obtained in the present study are described in Table 3. The total suspended sediment

Table 3 - Nutrients load in the lower São Francisco estimated for February and July 2014 at the anchor station (EF0).

Months	Parameter	Average concentration	Average monthly flow (m^3/s)	Daily loads (T/day)	Monthly loads (T/Month)
February	TSS	4.32 mg.L^{-1}	1262.06	471.06	13189.70
	SiO_4	4.20 mg.L^{-1}		458.26	12831.37
	PO_4^{-3}	1.38 μg L^{-1}		0.15	4.22
	HPO_4^{-2}	13.29 μg L^{-1}		1.45	40.57
	NID	30.70 μg L^{-1}		3.35	93.73
July	TSS	11.57 mg.L^{-1}	1164.00	1164.15	36088.56
	SiO4	3.59 mg.L^{-1}		361.28	11199.71
	PO_4^{-3}	3.70 μg L^{-1}		0.37	11.54
	HPO_4^{-2}	14.72 μg L^{-1}		1.48	45.90
	NID	83.64 μg L^{-1}		8.41	260.84

fluxes were estimated at about 13189.70 T/month and 36088.56 T/month in February and July 2014, respectively. The highest value in the rainy season (July) can be associated with more sendiment inputs from soil material originated from the eroded banks due to the high precipitation and carried to the estuary by runoff (Medeiros *et al.*, 2016), and are in agreement with TSS fluxes reported by Medeiros *et al.* (2007) during intense operation of Xingó (due to the electricity crisis). However, when compared to the pre-crisis months (April 2001) and the recovery period (February to March 2002) the total flows of suspended solids obtained in 2014 were lower than what was reported by Santos (1993) with 2,100.000 tons and Milliman (1975) with 6,900.000 tons.

In details, contrary to the other nutrients, silicate showed higher values during the dry period (February) with 12831.37 T/month, against 11199.71 T/month in July (Table 3). Our results were below the estimates presented in Medeiros *et al.* (2011b) where it was found average values of 25,000 T/month, with maximum of about 68,000 T/month. Similarly, Santos (1993) estimated a total load of about 650,000 T/month for the hydrological years of 1983 and 1984. This is an important finding as it might be associated with the role played by the basal fluxes overcoming the surficial runoff and the lesser consumption by the diatomaceous (Knoppers *et al.*, 2016).

The estimates for phosphorus, total phosphorus and NID were 4.22 T/month, 40.57 T/month, 93.73 T/month in February, and 11.54 T/month, 45.90 T/month, 260.84 T/month, respectively. These results are in agreement with those found in Medeiros *et al.* (2011b), although the authors also indicated that between November 2000 and March 2002, there have been higher values of these nutrients in the SF estuary. In addition, the NID loads in our study were below that reported by Santos (1993) where was observed values of 69,600 tons.

5. Conclusions

Using both in situ field measurements in February and July 2014, and river discharge, precipitation rates, we estimated the nutrients concentration variability in the SF estuary and investigated the potential role of outflow discharges, circulation and precipitation on nutrients fluxes exchange. The small difference in the streamflow between February (1,160 m^3/s) and July (1,260 m^3/s), reflected the minor role of the river discharge on the variability of the nutrients load in the estuary. On the other hand, we showed evidences that the high precipitation in July 2014, may have contributed to enhancing the sediment budge towards the estuary mouth reflected in the increased sediment loads from February (13189.70 T/month) to July 2014 (36088.56 T/month). We found substantial variability in current velocity within the estuary main channel, which indeed altered the internal circulation and generated a stronger water exchange between the estuary and the coast in July (~0.9 m/s) compared to February 2014 (~0.7 m/s). This study also found that except for silicates, there was an increase in the nutrients load transported to the estuary from February to July 2014. An important finding was the suggestion of presence of basal fluxes overcoming the surficial runoff which justified the opposite results of silicates load with higher fluxes in February (12831.37 T/month), against 11199.71 T/month in July. Overall, the absence of strong variability in fluvial discharge and similar tide ranges, resulted in their small influence on the nutrients load estimation. In summary, the local precipitation and internal circulation not only were the main factors responsables for the nutrients load variability within the estuary, but also may contributed to remebolize the suspended sediment from the river margens.

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