Acta Limnologica Brasiliensia

Publication of the Brazilian Association of Limnology

Original Article
Acta Limnologica Brasiliensia, 2016, vol. 28, e21
http://dx.doi.org/10.1590/S2179-975X3416
ISSN 0102-6712

Nutrient behavior in a highly-eutrophicated tropical estuarine system

Comportamento de nutrientes em um sistema estuarino tropical altamente eutrofizado

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Cite as: Brandini, N. et al. Nutrient behavior in a highly-eutrophicated tropical estuarine system. *Acta Limnologica Brasiliensia,* 2016, vol. 28, e-21.

Abstract: Aim: There are few studies dealing with the biogeochemical processes occurring in small estuaries receiving high sewage loading in tropical regions. The aim of this investigation was to characterize the biogeochemical behavior of nutrients in superficial waters collected at the Iguaçu estuarine system, during specific conditions (neap tide), located at the inner sector of a heavily eutrophicated embayment (Guanabara Bay, SE Brazil). **Methods:** Physical and chemical variables were measured in situ (pH, temperature, conductivity, salinity, total dissolved solids, transparency, dissolved oxygen), whereas suspended particulate matter, chlorophyll *a*, phaepigments and nutrients (carbon, nitrogen and phosphorus forms) were measured in laboratory across the mesohaline estuarine gradient. **Results:** The Iguaçu River mouth is in a high stage of eutrophication, considering nutrient concentrations, chlorophyll *a* and transparency of water column. Results indicate a transition from heterotrophic conditions to autotrophic conditions, since the nutrients concentrations showed a decreasing pattern along the saline gradient, while the chlorophyll an increased over the transects. The pH values and chlorophyll : phaeopigments ratios are significantly related to the amount and quality of organic matter contents, especially at transects under strong marine influence. More than 95% of the dissolved and total nitrogen concentrations are represented by NH_4^+ contributions, which are related to the ammonification of organic matter contents in this region, indicating the existence of untreated sewage loads in this area. **Conclusion:** In this study, the Iguaçu River seemed to contribute with high inputs of nutrients that support important phytoplankton production at the inner regions of the bay related to the CO_2 sink and autotrophic metabolism, showing the importance of verifying the biogeochemical behaviors of nutrients in estuarine areas, even in small scale.

Keywords: Iguaçu River; estuary; nitrogen; eutrophication; phosphorus.

Resumo: Objetivo: Existem poucos estudos que tratam dos processos que ocorrem em pequenos estuários que recebem uma elevada carga de matéria orgânica em regiões tropicais. O objetivo do presente trabalho foi caracterizar o comportamento biogeoquímico de nutrientes presentes em água superficial da foz do rio Iguaçu, durante condições específicas (maré de quadratura, vazante), localizado no setor interno de uma baía altamente eutrofizada (baía de Guanabara, SE Brasil). **Métodos:** Variáveis físicas e químicas foram medidas *in situ* (pH, temperatura, condutividade, salinidade, total de sólidos dissolvidos, transparência, oxigênio dissolvido), já o material particulado em suspensão, clorofila *a* e os nutrientes (carbono e as formas de nitrogênio e fósforo) foram medidos em laboratório, ao longo de um gradiente estuarino mesohalino. **Resultados:** A foz do rio Iguaçu está em alto estágio de eutrofização, considerando-se as concentrações de nutrientes, clorofila *a* e de transparência da coluna d' água encontrados. Os resultados indicam uma transição de condições heterotróficas para autotróficas, visto que as concentrações dos nutrientes diminuíram ao longo do gradiente salino, enquanto a clorofila *a* aumentou ao longo dos transecções. O pH e a razão clorofila : feopigmentos estiveram relacionados com a quantidade e qualidade da matéria orgânica em decomposição, sobretudo nos transecções sob maior influência marinha. Mais de 95% do nitrogênio dissolvido estava na forma de amônio (NH_4^+), proveniente do processo de amonificação da matéria orgânica em excesso na região, indicando presença de esgoto sem tratamento. **Conclusão:** Neste estudo, o rio Iguaçu contribuiu com altas cargas de nutrientes que suportam uma importante produção primária na região interna da baía, estando relacionada à absorção de CO_2 e metabolismo autotrófico, mostrando a importância de se identificar os comportamentos biogeoquímicos de nutrientes em áreas estuarinas, mesmo em pequena escala.

Palavras-chave: rio Iguaçu; estuário; nitrogênio; eutrofização; fósforo.

1. Introduction

Estuaries are characterized by the mixture of fresh and salt water, can be rich in organic matter and nutrients, capable of sustain large populations of detritivores and primary consumers. These systems support ecologically and economically important animal populations, including birds and fishes (Boyes & Elliott, 2006). The internal regions of estuaries receive different materials from continental drainage, which suffer physical-chemical processes like adsorption and/or desorption, input and/or removal due to marine water mixing with river water (e.g., changing salinity, pH and turbidity) and biological removal processes by phytoplankton (Knoppers et al., 2006; Pritchard & Schubel, 1981). The variability and intensity of these processes are affected by the seasonality and which is primarily regulated by river discharge, especially in tropical regions (Knoppers & Kjerfve, 1999; Sant'Anna et al., 2007).

During the last decades, the coastal region of Rio de Janeiro city (SE Brazil) has suffered the release of domestic wastes and industrial effluents on coastal waters. These impacts are accelerating the eutrophication processes and the contamination by toxic metals of aquatic ecosystems. This region is considered as one of the major examples of coastal degradation in Brazil, in relation to both organic and inorganic contaminants loading (Kjerfve et al., 1997; Knoppers & Kjerfve, 1999; Crapez et al., 2000; Borges et al., 2009; Aguiar et al., 2011; Meniconi, 2012; Paranhos & Andrade, 2012; Cotovicz Junior et al., 2015).

The spatial variability of nutrients biogeochemistry in estuaries is directly associated to fluvial contributions, forming a well-defined salinity gradient, influencing deeply the estuarine circulation and affecting the biological and biogeochemical processes (Day et al., 1989). The changes on pH, turbidity and ecosystem metabolism during the fresh and salt waters mixing contribute directly to determine nutrient behaviors (Knoppers et al., 2006). This occurs, for example, within shallow estuarine waters, where tidal variations can be an important factor of horizontal and vertical mixing. This factor can increase the primary production rates of surface waters, due to the mineralization of nutrients by benthic organisms (Nixon, 1981) and the regeneration to the water column.

Materials from fluvial contributions are transported and transformed during their way along the estuarine waters (Burton & Liss, 1976; Head, 1985; Morris, 1985). One of the classic methods to identify gains and losses of these materials in estuaries, allowing the identification and the dimensioning of transformation spots across the mixing zones, consists in plotting the concentrations of a chemical species of interest in function of the salinity gradient. The concentrations distribution in relation to dilution theory can be of concave shape, indicating material loss (sinking process) during dilution, or present a convex shape, suggesting material gain (where the area acts as a source) in the system (Liss, 1976; Head, 1985).

The estuaries are generally sinks for detritus that comes from river waters. The physical-chemical processes of water and molecules interactions vary in function of salinity (conservative behavior), being responsible for the acceleration of organic matter mineralization process or even increasing primary production, occurring with higher intensity at areas between 0 and 15 of salinity (Morris, 1985; Turner & Millward, 2000, 2002).

The main processes that regulate sources and sinks character of elements in the estuary are:

i) advective and diffuse fluxes; ii) physical-chemical reactions (precipitation, adsorption, desorption and flocculation); iii) biological assimilation and denitrification; and iv) organic matter degradation and excretion (Pritchard & Schubel, 1981). The present work evaluated the nutrients biogeochemical behavior in superficial waters from the Iguaçu estuary, during specific conditions (neap tide), located at the inner sector of a eutrophic embayment (Guanabara Bay-RJ), over a salinity gradient. This specific condition was chosen in order to observe processes during the period of lower dilution of the freshwater from Iguaçu River into marine Guanabara Bay waters. The hypothesis is that Iguaçu River estuarine area is an important region to nutrients transformations, working as a sink.

2. Material and Methods

2.1. Study area

The Guanabara Bay is one of the largest bays of Brazil (381 km²) and receives contributions from around 35 rivers, with mean flow of 131 $m^3 s^{-1}$ (Kjerfve et al., 1997). Most part of the drainage area (total of 4,000km²) presents high levels of pollutants released by domestic and industrial effluents (treated and untreated), from a 10 million population and around 10,000 industries (Pereira & Gomes, 2002). This results on a total discharge of domestic waste around 22.4 $m^3 s^{-1}$ (Silveira et al., 2011), which represents 75% of the organic pollution volume for the bay (Pereira & Gomes, 2002). Its internal areas (northwest and west) are classified as eutrophic or hypereutrophic, due to the large input of domestic wastes (mainly untreated) (Ribeiro & Kjerfve, 2002). The high availability of nutrients, strong radiation intensity and thermal stratification promotes huge phytoplankton development and a net CO_2 sink at air-water interface, which ranged between -9.6 and -18.3 mol C $m^{-2} yr^{-1}$ (Cotovicz Junior et al., 2015).

Iguaçu River is an important contributor of organic loads to the bay. The superficial water has biochemical oxygen demand above 10 mg L^{-1}, reaching almost 20 mg L^{-1} at the river's mouth (Silveira et al., 2011). The Iguaçu River has 726 km² of drainage basin, with mean water flow of 20.0 $m^3 s^{-1}$ during dry season, corresponding approximately 17% of the continental contribution to Guanabara Bay (JICA, 2003). Some major problems of the Iguaçu River watershed are: (i) absence of urban structure; (ii) deficiency or total inexistence of sewage treatment and garbage collection; (iii) deforestation of river springs, with disorderly and illegal occupation of rivers margins; (iv) silting at the river mouth (Meniconi, 2012).

2.2. Sampling

Four perpendicular transects were established along the mouth of Iguaçu River (≈ 1.5 km), with 3 sampling points in each transect (located on the left and right margins, and at an intermediate position). The sampling was performed in April 2011 (Figure 1), during the ebbing period of a neap tide. This scenario was chosen to ensure that the water fluxes and their associated nutrients were unidirectional and continuous and, especially, to observe processes during the period of lower dilution of the freshwater into Guanabara Bay waters. The historical mean of precipitation on April is 25mm. The accumulated precipitation during March 2011 (30 days before the sampling) was 202.7mm and for the week before the sampling, the accumulated precipitation was 113 mm, being higher than the historical mean for this area (ICEA, 2013). Since the sampling was after a rainy week, it guaranteed a higher flux of freshwater to the estuarine region, supporting the study of the influence of Iguaçu River freshwaters at the estuarine region, at the meeting with Guanabara Bay.

At the sampling stations, superficial water samples were collected using previously decontaminated polyethylene bottles. The samples were stored in a cooler with ice until processing. At the laboratory, the water samples were filtered (glass fiber filters GF/F - Whatman) and frozen until chemical analysis.

2.3. Physical-chemical, pigments and nutrients determinations

The physical-chemical parameters were measured *in situ* using a portable multiparametric probe (Hanna) for temperature, depth, pH, dissolved oxygen (DO), transparency, conductivity, total dissolved solids (TDS) and salinity. Total dissolved carbon was measured using a catalytic oxidation reaction under high temperature in a Schimadzu TOC Vcph. Suspended particulate matter (SPM) contents were estimated by gravimetry. The chlorophyll *a* and phaeopigments contents were measured on the material obtained by filtration with glass fiber filters Whatman GF/F (ϕ = 47 mm), using an extraction with acetone 90% (Strickland & Parsons, 1972). Total nitrogen and total phosphorus concentrations were obtained

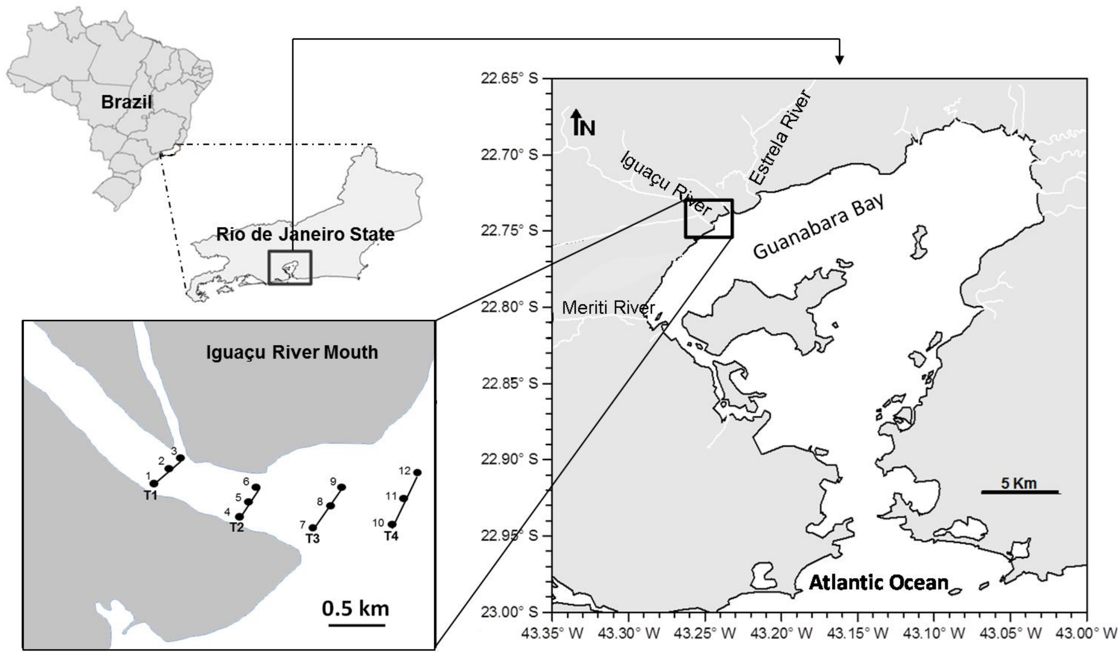

Figure 1. Transects at the mouth of Iguaçu River, northwestern sector of Guanabara bay-Rio de Janeiro, Brazil. T1: transect 1; T2: transect 2; T3: transect 3; T4: transect 4.

by persulfate oxidation (Aspila et al., 1976). The dissolved nutrient forms (phosphate, nitrite, nitrate, ammonia) were measured in the previously filtered water samples, by colorimetric methods described by Grasshoff et al. (1999), using a SHIMADZU spectrophotometer model UV-1601.

2.4. Statistical analyses

Initially, linear models were used to determine the data normality. We used the non-parametric Kruskal-Wallis test to compare the averages of the parameters between the transects, since that the results do not follows a normal distribution. The correlations between the variables were calculated with the Spearman coefficient. The STATISTICA 6.0 program was applied to all statistical analysis (based on $p<0.05$) (Zar, 1999).

3. Results

The electrical conductivity showed conservative behavior and it expresses indirectly the ions concentration (Cl^-, SO_4^{-2}, SO_3^-, HCO_3, CO_3^-, NO_3^- e NO_2) (Table 1). The suspended particulate matter (SPM), pH and DO had a clear trend of increase on the direction of the river mouth, following the increase of salinity (Table 2; Figure 2).

The temperature, transparency, suspended particulate matter, total dissolved carbon and organic phosphorus did not show linear variations in relation to salinity. The dissolved oxygen, SPM and chlorophyll *a* presented an inverse behavior compared to nutrients (with the exceptions of NO_2 and NO_3), probably being related to increases on primary production at mainly transects 3 and 4 (Figures 2 and 3). The nitrite, ammonium, dissolved inorganic nitrogen, nitrogen : phosphorus ratio (N:P), total nitrogen, chlorophyll *a* and phaeopigments in superficial water were significantly different between transects (Table 2), being transect 1 with lower pH and salinity when compared to transect 4, more distant from river mouth (the distance between transects 1 and 4 is 2 km (Table 1; Figure 2).

It was also observed an increase of chlorophyll *a* values (assimilation process) and increase of water transparency (allowing high radiation intensity to the surface waters stimulating the primary production) (Figure 4; Table 3), despite the own dilution process by saline waters. Also there is a positive tendency between SPM and chlorophyll *a*, possibly explained by the higher primary productivity producing more SPM (Figure 4; Table 3). The dissolved inorganic nitrogen and phosphorus ratio were always above Redfield proposal – 16:1 (Redfield, 1958; Golterman & Oude, 1991), with no defined spatial pattern (Figure 5).

Table 1. Mean and standard deviation of physical-chemical and nutrient concentrations in superficial waters of Iguaçu River mouth, Guanabara bay-RJ.

Parameters	Transect 1	Transect 2	Transect 3	Transect 4
Depth (m)	2.2±1.5	1.8±1.2	1.2±1.2	1.7±0.3
Secchi (m)	0.20±0.16	0.83±0.29	0.50±0.0	1.67±0.29 [a]
pH	6.8±0.2	7.3±0.1	7.6±0.3	8.2±0.4 [a]
Salinity	1.7±0.6	5.0±1.0	7.5±0.9	10.0±1.0 [a]
Conductivity (mS cm^{-1})	1.8±1.1	6.3±1.4	7.7±1.2	9.9±1.4 [a]
DO (mg L^{-1})	2.3±0.5	4.4±1.2	6.1±1.6	9.1±2.0 [a]
DO (%)	29.4±5.8	56.1 ±15.6	77.6 ±20.1	116.6±26.5 [a]
Temperature (°C)	27.3±0.3	27.9±0.4	27.5±0.1	27.7±0.1
PO_4^{-2} (μM)	7.3±1.0	7.4±0.4	5.4±1.4	3.4±0.7
NO_2 (μM)	0.4±0.0	0.8±0.2	1.3±0.5	1.9±0.2 [a]
NO_3^- (μM)	0.1±0.0	0.6±0.4	1.7±1.5	2.8±0.6 [a]
NH_4^+ (μM)	225.3±7.9	181.6±21.6	156.9±31.5	119.3±28.9 [a]
DIN (μM)	225.8±7.9	183.0±22.0	160.0±29.6	124.0±28.1 [a]
DIN:DIP Ratio	31.2±3.4	24.8±4.1	30.0±3.0	36.7±1.1 [b]
TN (μM)	392.4±6.1	316.8±2.2	267.6±63.2	139.3±62.2 [a]
TP (μM)	17.9±3.1	13.1±0.9	12.4±3.0	9.4±1.0 [a]
ON (μM)	166.6±53.1	133.8±21.2	107.6±35.2	15.3±34.4
OP (μM)	10.6±2.1	5.7±1.1	7.0±1.6	6.0±0.4
TDC (mg L^{-1})	11.3±2.9	12.8±2.8	10.2±3.9	11.5±2.7
SPM (mg L^{-1})	16.1±9.0	7.5±4.4	9.4±2.5	19.8±8.2
Chl-a (μg L^{-1})	10.3±2.9	28.3±6.4	61.8±26.3	82.8±40.8 [a]
Phae (μg L^{-1})	29.9±8.0	72.6±15.7	153.0±60.1	214.6±103.8 [a]
Chl-a : Phae	0.35±0.01	0.39±0.01	0.40±0.01 [a]	0.38±0.00

Dissolved Oxygen (DO); Phosphate (PO_4^{-2}); Nitrite (NO_2); Nitrate (NO_3^-); Ammonium (NH_4^+); Total Dissolved Nitrogen (DIN); Total and Organic Nitrogen and Phosphate (TN; TP and ON; OP); Total Dissolved Carbon (TDC); Suspended Particulate Matter (SPM); Chlorophyll *a* (Chl-a); Phaeopigments (Phae) and Chlorophyll : Phaeopigments ratio. [a] Values are significantly different from transect 1 (Kruskal-Wallis; p<0.05). [b] Values are significantly different from transect 2 (Kruskal-Wallis; p<0.05).

Table 2. Significant variations found between the sampling transects at Iguaçu River's mouth (Guanabara bay-RJ), according to Kruskal-Wallis H test (3; n=12).

Transects	*Variables*	*H*	*p*
1 x 3	*Chl-a : Phae*	2.83	0.027
1 x 4	*Salinity*	3.06	0.013
	Secchi	3.06	0.013
	Conductivity	3.00	0.016
	pH	2.89	0.023
	DO	2.94	0.019
	DO %	2.94	0.019
	NO_2	2.94	0.019
	NO_3^-	2.83	0.027
	NH_4^+	2.94	0.019
	DIN	2.94	0.019
	TP	2.89	0.023
	TN	3.06	0.013
	Chlorophyll a	2.77	0.033
	Phaeopigments	2.83	0.027
2 x 4	*N:P*	3.06	0.013

Additionally, the trophic state of this environment was evaluated using as base the classifications of Organization for Economic Cooperation and Development (OECD, 1982), Vollenweider & Kerekes (1982) and Environmental European Agency (EEA, 1999). The Iguaçu River mouth showed the worst classifications of trophic state for the three different analyzed indexes (eutrophic and hypereutrophic), indicating that this system is on a high stage of eutrophication, considering nutrient concentrations, chlorophyll *a* and transparency of water column. The indexes were calculated using single parameters (Table 4).

When the eutrophication status is evaluated considering the Brazilian legislation (CONAMA resolutions, numbers 357/2005 and 430/2011) (Brasil, 2005, 2011), which established quality standards for superficial waters and for effluents released on aquatic ecosystems, the Iguaçu River mouth could be classified as a lotic environment of estuarine waters (salinity higher than 0.5 and lower than 30), with ammonia concentrations 2-4 times higher and total phosphorus concentrations 1.5-3 times higher than the established limits for this type of ecosystem. The oxygen levels at transects 1 and 2 are below the minimum values considered as healthy for human consumption

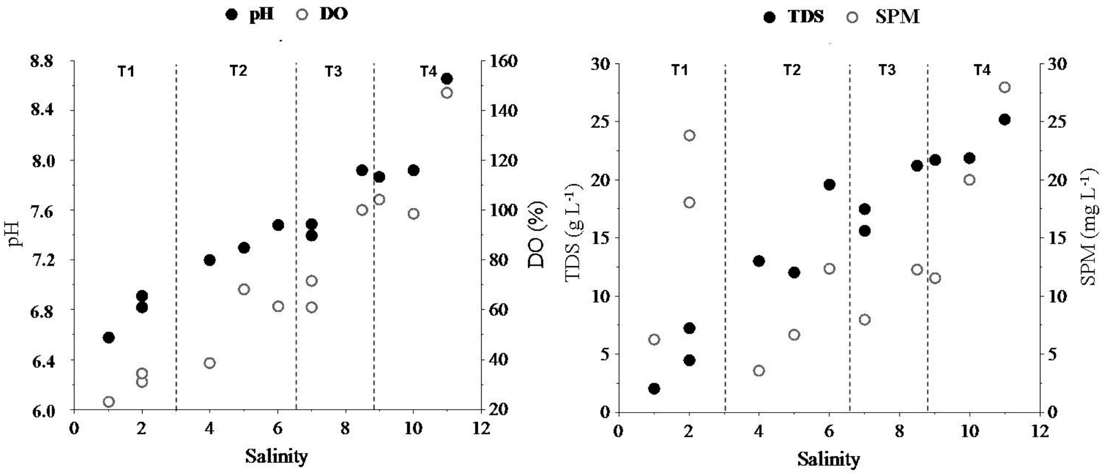

Figure 2. Mixture diagram (p<0.95 Conf. Int.) of pH, dissolved oxygen, total dissolved solids and suspended particulate matter, at Iguaçu River mouth in a salinity gradient from 0 to 12, Guanabara bay, Rio de Janeiro State, Brazil. T1: transect 1; T2: transect 2; T3: transect 3; T4: transect 4.

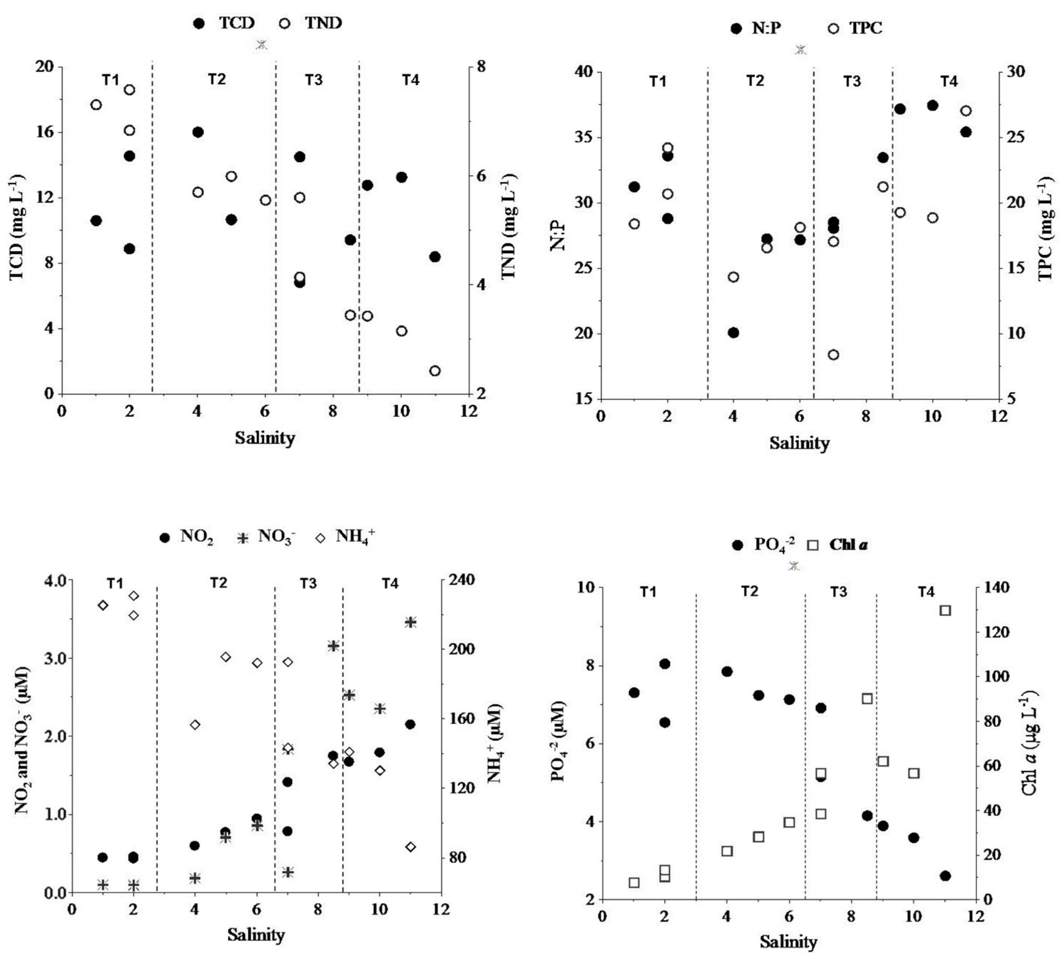

Figure 3. Mixture diagram (p<0.95 Conf. Int.) of dissolved inorganic nutrient: nitrite (NO_2), nitrate (NO_3^-), ammonium (NH_4^+) and phosphorus (PO_4^{-2}) and chlorophyll *a* (Chl-a), at Iguaçu River mouth in a salinity gradient from 0 to 12, Guanabara bay, Rio de Janeiro State, Brazil. T1: transect 1; T2: transect 2; T3: transect 3; T4: transect 4.

Table 3. Correlations found for all studied variables of the twelve sampling stations at Iguaçu River estuarine zone, using Spearman test ($p<0.05$).

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
1. Temperature	1.0	0.5	-0.4	***0.6***	0.4	0.5	0.5	0.5	0.5	-0.4	-0.4	-0.1	-0.3	-0.4	-0.5	-0.5	-0.4	0.1	0.4	0.4	0.5	-0.1
2. Salinity	0.5	1.0	-0.2	***0.8***	***1.0***	***0.9***	***1.0***	***1.0***	***0.9***	***-0.9***	***-0.9***	0.5	***-0.9***	***-0.9***	***-0.6***	***-0.9***	***-0.9***	-0.2	***1.0***	***1.0***	0.5	0.4
3. Depth	-0.4	-0.2	1.0	0.0	-0.2	-0.2	-0.2	-0.2	-0.3	0.1	0.2	-0.1	0.1	0.1	-0.1	0.2	0.2	0.0	-0.3	-0.3	-0.5	0.3
4. Secchi	***0.6***	***0.8***	0.0	1.0	***0.8***	***0.8***	***0.8***	***0.8***	***0.7***	***-0.8***	***-0.8***	0.3	***-0.6***	***-0.8***	***-0.8***	***-0.8***	***-0.7***	0.2	***0.7***	***0.7***	0.2	0.3
5. pH	0.4	***1.0***	-0.2	***0.8***	1.0	***1.0***	***1.0***	***1.0***	***1.0***	***-0.9***	***-0.9***	0.5	***-0.9***	***-0.9***	***-0.7***	***-0.9***	***-0.9***	-0.3	***1.0***	***1.0***	0.5	0.4
6. DO	0.5	***0.9***	-0.2	***0.8***	***1.0***	1.0	***0.9***	***0.9***	***1.0***	***-0.9***	***-0.9***	0.5	***-0.9***	***-0.9***	***-0.6***	***-0.9***	***-0.9***	-0.3	***1.0***	***1.0***	0.6	0.3
7. Conductivity	0.5	***1.0***	-0.2	***0.8***	***1.0***	***0.9***	1.0	***1.0***	***1.0***	***-0.9***	***-0.9***	0.5	***-0.9***	***-0.9***	***-0.7***	***-0.9***	***-0.9***	-0.2	***0.9***	***1.0***	0.5	0.4
8. NO_2	0.5	***1.0***	-0.2	***0.8***	***1.0***	***0.9***	***1.0***	1.0	***1.0***	***-1.0***	***-1.0***	0.5	***-0.9***	***-0.9***	***-0.7***	***-0.9***	***-0.9***	-0.3	***1.0***	***1.0***	0.5	0.3
9. NO_3^-	0.5	***0.9***	-0.3	***0.7***	***1.0***	***1.0***	***1.0***	***1.0***	1.0	***-0.9***	***-0.9***	0.4	***-0.9***	***-0.9***	***-0.6***	***-0.9***	***-0.9***	-0.4	***1.0***	***1.0***	***0.6***	0.3
10. NH_4^+	-0.4	***-0.9***	0.1	***-0.8***	***-0.9***	***-0.9***	***-0.9***	***-1.0***	***-0.9***	1.0	***1.0***	-0.4	***0.8***	***1.0***	***0.8***	***1.0***	***0.9***	0.2	***-0.9***	***-0.9***	-0.4	-0.3
11. DIN	-0.4	***-0.9***	0.2	***-0.8***	***-0.9***	***-0.9***	***-0.9***	***-1.0***	***-0.9***	***1.0***	1.0	-0.4	***0.8***	***1.0***	***0.7***	***1.0***	***0.8***	0.2	***-0.9***	***-0.9***	-0.4	-0.2
12. DIN:DIP	-0.1	0.5	-0.1	0.3	0.5	0.5	0.5	0.5	0.4	-0.4	-0.4	1.0	***-0.7***	-0.4	0.1	-0.5	-0.5	-0.3	0.4	0.4	-0.3	0.6
13. PO_4^{-2}	-0.3	***-0.9***	0.1	***-0.6***	***-0.9***	***-0.9***	***-0.9***	***-0.9***	***-0.9***	***0.8***	***0.8***	***-0.7***	1.0	***0.8***	0.4	***0.8***	***0.9***	0.5	***-0.9***	***-0.9***	-0.3	-0.5
14. TP	-0.4	***-0.9***	0.1	***-0.8***	***-0.9***	***-0.9***	***-0.9***	***-0.9***	***-0.9***	***1.0***	***1.0***	-0.4	***0.8***	1.0	***0.8***	***1.0***	***0.9***	0.3	***-0.9***	***-0.9***	-0.4	-0.3
15. OP	-0.5	***-0.6***	-0.1	***-0.8***	***-0.7***	***-0.6***	***-0.7***	***-0.7***	***-0.6***	***0.8***	***0.7***	0.1	0.4	***0.8***	1.0	***0.7***	0.5	0.0	***-0.6***	***-0.6***	-0.3	0.0
16. TN	-0.5	***-0.9***	0.2	***-0.8***	***-0.9***	***-0.9***	***-0.9***	***-0.9***	***-0.9***	***1.0***	***1.0***	-0.5	***0.8***	***1.0***	***0.7***	1.0	***0.9***	0.3	***-0.9***	***-0.9***	-0.4	-0.2
17. ON	-0.4	***-0.9***	0.2	***-0.7***	***-0.9***	***-0.9***	***-0.9***	***-0.9***	***-0.9***	***0.9***	***0.8***	-0.5	***0.9***	***0.9***	0.5	***0.9***	1.0	0.3	***-0.9***	***-0.9***	-0.5	-0.2
18. TDC	0.1	-0.2	0.0	0.2	-0.3	-0.3	-0.2	-0.3	-0.4	0.2	0.2	-0.3	0.5	0.3	0.0	0.3	0.3	1.0	-0.3	-0.3	-0.3	-0.1
19. Chl-a	0.4	***1.0***	-0.3	***0.7***	***1.0***	***1.0***	***0.9***	***1.0***	***1.0***	***-0.9***	***-0.9***	0.4	***-0.9***	***-0.9***	***-0.6***	***-0.9***	***-0.9***	-0.3	1.0	***1.0***	***0.6***	0.3
20. Phae	0.4	***1.0***	-0.3	***0.7***	***1.0***	***1.0***	***1.0***	***1.0***	***1.0***	***-0.9***	***-0.9***	0.4	***-0.9***	***-0.9***	***-0.6***	***-0.9***	***-0.9***	-0.3	***1.0***	1.0	***0.6***	0.3
21. Chl-a : Phae	0.5	0.5	-0.5	0.2	0.5	0.6	0.5	0.5	***0.6***	-0.4	-0.4	-0.3	-0.3	-0.4	-0.3	-0.4	-0.5	-0.3	***0.6***	***0.6***	1.0	-0.2
22. SPM	-0.1	0.4	0.3	0.3	0.4	0.3	0.4	0.3	0.3	-0.3	-0.2	0.6	-0.5	-0.3	0.0	-0.2	-0.2	-0.1	0.3	0.3	-0.2	1.0

Dissolved Oxygen (DO); Phosphate (PO_4^{-2}); Nitrite (NO_2); Nitrate (NO_3^-); Ammonium (NH_4^+); Total Dissolved Nitrogen (DIN); Total and Organic Nitrogen and Phosphate (TN; TP and ON; OP); Total Dissolved Carbon (TDC); Suspended Particulate Matter (SPM); Chlorophyll *a* (Chl-a); Phaeopigments (Phae) and Chlorophyll : Phaeopigments ratio.

after conventional treatment (5 mg L⁻¹; Brasil, 2005). These dissolved oxygen concentrations were measured during the day, so at night, when respiration and decomposition processes prevail these concentrations could be lower (Odum & Barret, 2011; Knoppers & Kjerfve, 1999).

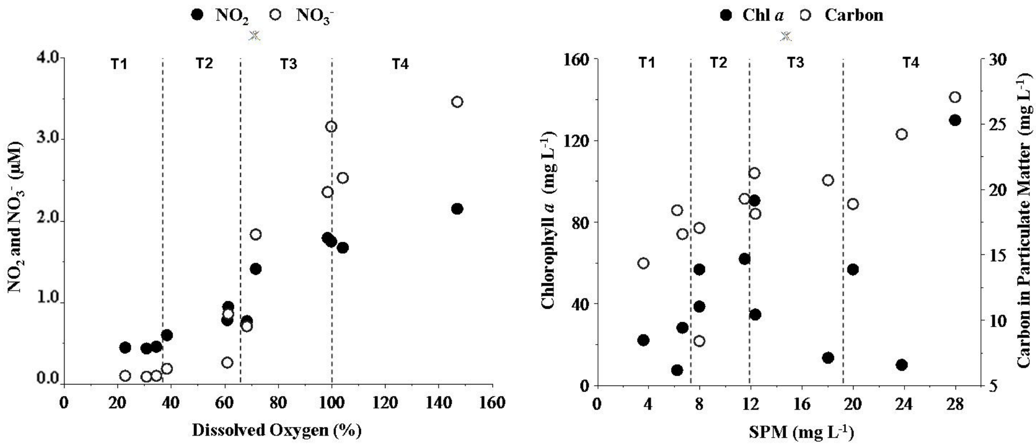

Figure 4. Relationship of dissolved inorganic nutrient: nitrite (NO_2), nitrate (NO_3^-) with dissolved oxygen and the relationship between chlorophyll *a* (Chl-a), carbon content in particulate matter and Suspended Particulate Matter (SPM), at Iguaçu River mouth, Guanabara bay, Rio de Janeiro State, Brazil. T1: transect 1; T2: transect 2; T3: transect 3; T4: transect 4.

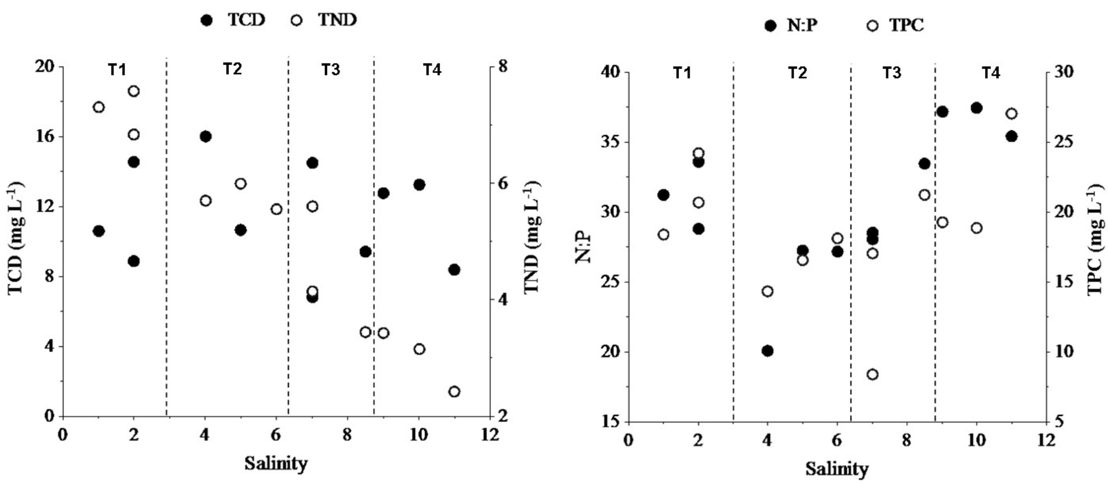

Figure 5. Mixture diagram of total dissolved carbon and nitrogen and nitrogen : phosphorus ratio and total particulate carbon, at Iguaçu River mouth in a salinity gradient from 0 to 12, Guanabara bay, Rio de Janeiro State, Brazil. T1: transect 1; T2: transect 2; T3: transect 3; T4: transect 4.

Table 4. Classification of trophic status of Iguaçu River mouth, Guanabara bay, using three different indexes established for marine and coastal environments, where TP= Total Phosphate, Chl-*a*= Chlorophyll *a*, DS= Depth of the Secchi, PID= dissolved inorganic phosphorus and NID= dissolved inorganic nitrogen.

	OECD [a] TP	OECD [a] Chl-*a*	OECD [a] DS	Vollenweider and Kerekes [b] TP	Vollenweider and Kerekes [b] Chl-*a*	EEA [c] DIP	EEA [c] DIN
Index	> 40µg L⁻¹	> 10µg L⁻¹	< 1.7 m	> 100µg L⁻¹	> 25µg L⁻¹	> 16 µM	> 1.1 µM
Transect 1	Eutrophic	Eutrophic	Eutrophic	Hypertrophic	Eutrophic	Eutrophic	Eutrophic
Transect 2	Eutrophic	Eutrophic	Eutrophic	Hypertrophic	Hypertrophic	Eutrophic	Eutrophic
Transect 3	Eutrophic	Eutrophic	Eutrophic	Hypertrophic	Hypertrophic	Eutrophic	Eutrophic
Transect 4	Eutrophic	Eutrophic	Eutrophic	Hypertrophic	Hypertrophic	Eutrophic	Eutrophic

[a] OECD (1982); [b] Vollenweider & Kerekes (1982); [c] EEA (1999).

4. Discussion

Generally, rivers waters have lower pH than marine waters, and when their mixture occurs, the tendency is a linear increase of the variable in function of salinity increase. Among the processes, the bicarbonate and carbonate occurrence (abundant in marine waters) influences on neutralization of H^+ ions, which increases pH values. Besides, pH also increases with high primary productivity, since phytoplankton community absorbs CO_2 from water for photosynthesis, as observed in this study. On the other hand, during organic matter decomposition, CO_2 is produced and decrease pH (Borges & Abril, 2011).

The temperature, transparency, suspended particulate matter, total dissolved carbon and organic phosphorus did not show linear variations related to salinity (non-conservative behavior). Physical processes (including possible sediment resuspension), intense recycling in water column and the fact that the bay waters are already eutrophic could explain the absence of linear variation of these parameters. Besides they may be influenced by differences on hydrodynamics and margins morphology, since each transect was composed by two stations at the margins (variation of depth on left margin: 0.5-2.5m; and, on right margin: 0.5-1.5m) and one station at the center of the transect, where the depth was always higher (variation of depth: 2.0-3.5m). Also, the differences on depths between transects, may have influenced mainly transparency and SPM results (Gunduz et al., 2011), as well as observed by Rodrigues et al. (2009), when they analyzed a gradient at Sepetiba bay, influenced by São Francisco River Channel.

In general, the spatial gradient of nutrients in this study did not follow the salinity gradient. This behavior suggests the assimilation of the nutrients along the salinity gradient by the phytoplankton community. In fact, the inner sectors of the bay were calculated as autotrophic where the production of organic matter is higher than the respiration, which corroborates to a possible SPM accumulation due to productivity, as observed in the present work (Cotovicz Junior et al., 2015).

For the total and dissolved phosphorus concentrations, the results suggest (1) the consumption of phosphorus for primary production, since chlorophyll *a* increases, (2) geochemical processes such as adsorption to particulate matter and precipitation of phosphorus and/or (3) a dilution of phosphorus along the estuarine gradient. The organic phosphorus concentrations decreased along the saline gradient, what may be related to the distance from organic matter sources, fast assimilation by phytoplankton community and/or remineralization by bacterial community (Zhang et al., 2008; Rodrigues et al., 2009; Gunduz et al., 2011).

A work conducted at the northwestern inner portion of Guanabara Bay confirmed the increasing of phosphorus flux to intertidal sediments to nearly 9-times higher than estimated values of the 1800s, which is in excellent agreement with the population growth in the drainage basin of the study area (Borges et al., 2009). At Rodrigo de Freitas Lagoon (Rio de Janeiro State-Brazil), the influence of sewage on the dynamics of phosphorus speciation described that organic carbon made up 43% of the sewage particulate and organic phosphorus, 1%. The dissolved phosphate, quickly consumed within 3 days by primary producers, was the largest fraction of total phosphorus in superficial water followed by particulate organic phosphorus (assimilated within 55 days). In this case, these phosphorus forms exceeded the uptake capacity of the system, leading to the formation of refractory organic matter (Carreira & Wagener, 1998).

The dissolved inorganic nitrogen and phosphorus ratio were always above Redfield proposal – 16:1 (Redfield, 1958; Golterman & Oude, 1991), with no defined spatial pattern (Figure 5). These results suggest that this area has tendency for phosphorus limitation. However, it seems to exist different trends to the N:P ratio considering stations with salinity under 3 (essentially freshwater), in comparison to the stations with higher salinities (when the bay's influence seems to be more effective). The N:P ratio is positively correlated when it is considered only the stations with low salinity (> 3), characterizing a conservative behavior and almost reaching the ratio of 16:1, as an effect of an improvement on primary production.

The positive correlation of NO_2^- and NO_3^- concentrations with salinity (Table 3) is an indicative of nitrification process due to dissolved oxygen increase caused by the mixture of water masses and higher photosynthetic rates (Figure 4). The negative correlation of NH_4^+ with salinity also corroborates this hypothesis, since the nitrification is an aerobic process of biological oxidation of NH_4^+ followed by the oxidation of NO_2 to NO_3^-, performed by specific groups of autotrophic bacteria. One part of this NH_4^+ can be also emitted to the atmosphere, since a previous study at Guanabara Bay quantified the emissions of NH_4^+ from water to the atmosphere and showed that these emissions were particularly important nearly of the most polluted regions of the bay, including the northwest area (Guimarães & Mello, 2006). Anyway the transect 1 showed a tendency to sub-oxic conditions (DO between 20-40% of saturation). As the DO levels were extremely low at this region, part of the OM could be decomposed using NO_3^- as oxidant agent, what could explain the low nitrate levels observed at this transect (Libes, 1992) (Figure 4).

At transect 1, the low DO saturation and high nutrients concentrations, in especial ammonium concentrations, indicating the influence of continental waters that are rich in inorganic and organic nutrients. This reflects the drainage basin discharge influence (including materials from rivers, mangrove channels and domestic wastes), characterizing the occurrence of reduced redox conditions (Lucas et al., 1999; Noriega et al., 2005). Bricker et al. (2003) remind that dissolved oxygen concentrations lower than 5 mg L^{-1} indicate the beginning of biological stress to several aquatic populations, especially for species with lower tolerance for anoxic conditions, including species at the top of food web. Some measured concentrations of dissolved oxygen were classified under hypoxic conditions, i.e. when DO is lower than 2 mg L^{-1}, and is considered one of the most threats to coastal waters worldwide (Diaz & Rosenberg, 2008). The expansion of hypoxic zones is associated with eutrophication (Conley et al., 2009).

Analyzing the proportions of nitrogen forms in relation to total nitrogen contribution, it was observed that 95% is present as NH_4^+, probably from the ammonification process of organic matter in excess at this area. Environments with high ammonia concentrations indicate the predominance of decomposers organisms and reducer processes, where dissolved oxygen is very low. Ammonia is a common constituent present in domestic wastes, as a result of urea hydrolysis and of the biological degradation of organic nitrogen compounds. It is interesting to highlight that ionized and non-ionized ammonia compounds are considered toxic to several aquatic organisms (Reis & Mendonça, 2009).

In this work, considering the processes observed over the salinity gradient suggest that this area works as sinks for nutrients (especially transects 3 and 4) and sources of phytoplankton biomass (indicated by high levels of phaeopigments and chlorophyll *a*), due to the increasing on an opportunistic primary production (Barrera-Alba et al., 2009; Cotovicz Junior et al., 2015;). In fact, the biogeochemical processes are, in most part, more intense at the maximum turbidity zone or also in waters between 0 and 10 of salinity (Lucas et al., 1999; Rodrigues et al., 2009). The pronounced gradient observed between 0 and 5 of salinity, where occurs most part of all transformations, was also observed by Morris et al. (1982) at Tamar estuary, South England.

Differences on biogeochemical processes in eutrophic and oligotrophic systems are also an interesting discussion issue. A study of six rivers in the south coast of Brazil showed that (i) total phosphorus concentrations were five times higher on rivers with urbanized areas in their drainage basin than on the three studied rivers under protection areas; (ii) about phosphorus speciation, there is a prevalence of the inorganic form of phosphorus over the organic one for urbanized rivers (eutrophic systems). In non-urbanized areas both concentrations of inorganic and organic forms kept constant (Pagliosa et al., 2005).

Different processes acting on the nutrients dynamics were described for the Patos Lagoon (south region of Brazil) along a salinity gradient. The dissolved nitrite, nitrate and phosphate was removed from water column in very low salinity (> 7), being totally depleted around a salinity of 5, as result of a high primary production, flocculation and particle scavenging. Within the higher salinity region of this lagoon (salinity: 13-18), the primary production was supported by regeneration of phosphate and nitrogen in the form of ammonium and the authors also suggests the organic matter remineralization, probably within the sediment column, as an important process to nutrients behavior in this zone (Windom et al., 1999).

The river plume of the Iguaçu River seems to be an important source of nutrients and primary producers to the inner regions of Guanabara Bay, since that high concentrations of chlorophyll *a* and huge phytoplankton blooms were described in previous studies and related to the high availability of nutrients provided by polluted rivers and effluent discharges especially in some of the most internal regions of the estuary (Ribeiro & Kjerfve, 2002; Cotovicz Junior et al., 2015; Oliveira et al., 2016). As described by Cotovicz Junior et al. (2015), the most confined part of the bay behaved as the "bloom genesis region" that can spread phytoplankton production for other sectors of the bay.

The distribution of most part of the constituents evaluated in this work is regulated by the mixing between river and bay waters along the transects, suggested here by salinity as proxy. The downstream region (higher salinity) seemed to work as sinks to nutrients, with a substantial increase on chlorophyll *a* on water. On the other hand, the low values obtained for DO pointed out the reduced character of transects 1 and 2, upstream sectors, usually observed in environments with advanced stage of eutrophication. The chlorophyll : phaeopigments ratio are related to the proportion on production and decomposition of organic matter, so the ratios under the unit observed for all the salinity gradient suggest a prevail of degradation. The main source of nutrients is composed by ammonium (higher than 95% of DIN), indicating a strong influence of untreated domestic wastes in this waters.

Summarizing, the nutrients concentrations showed a decreasing pattern along the saline gradient. The total and inorganic nutrients behavior suggest a relationship with primary production, in other words, the nutrients are assimilated along the saline gradient, and this incorporation reflects the chlorophyll *a* increasing on water column, besides there is the dilution on sea water, which contributes to decreasing the nutrients concentrations. The studied variables denoted that in the transects 1 and 2 the respiration is more pronounced (low levels of dissolved oxygen and chlorophyll *a*), while in the transects 3 and 4 the photosynthesis dominated (high oxygen and chlorophyll *a* levels). Despite the fact that this work did not performed assessment of system metabolism, the results seems to indicate one transition from heterotrophic conditions (sectors 1 and 2) to autotrophic conditions (sectors 3 and 4). The trophic status analysis indicated that this area is a eutrophic to hypereutrophic environment, in other words, presents an advanced status of eutrophication. Comparing the trophic status with other estuaries worldwide, the estuarine plume of Iguaçu River is classified in the worst conditions of eutrophication and environmental quality.

It is important to point out that there are 35 rivers and streams in the Guanabara Bay drainage basin and among them only six contribute to significant volumes of freshwater to the bay, one of them is Iguaçu River. It is necessary to investigate biogeochemical processes in those estuarine areas, since the same biogeochemical behavior observed at Iguaçu River could be extended to other polluted rivers that flow into the bay, such as Meriti and Estrela Rivers. This work highlights the importance of understanding the nutrients dynamics in small scale studies, especially at areas in this gradient of salinity (0-10), in order to understand the dynamics of the nutrients that come from continental sources and their effective contribution to the biogeochemistry of estuarine zones. In this case, this small polluted river seems to contribute with high inputs of nutrients that support important phytoplankton production at the inner regions of the bay related to the CO_2 sink and autotrophic metabolism, as described by Cotovicz Junior et al. (2015). Besides these areas are vulnerable to resuspension impacts due to dredging activities, since actually there are projects for the Guanabara bay drainage basin recuperation that include this kind of activity at rivers mouths.

Acknowledgements

The authors would like to thank CAPES for financial support (process number 0247/08-1) and CNPq for the productivity sponsors.

References

AGUIAR, V.M.C., BAPTISTA-NETO, J.A. and RANGEL, C.M. Eutrophication and hypoxia in four streams discharging in Guanabara Bay, RJ, Brazil, a case study. *Marine Pollution Bulletin*, 2011, 62(8), 1915-1919. PMid:21708390. http://dx.doi.org/10.1016/j.marpolbul.2011.04.035.

ASPILA, K.I., AGEMIAN, H. and CHAU, A.S.Y. A semi-automated method for the determination of inorganic, organic and total phosphate in sediments. *Analyst*, 1976, 101(1200), 187-197. PMid:1259177. http://dx.doi.org/10.1039/an9760100187.

BARRERA-ALBA, J.J., GIANESELLA, S.M.F., MOSER, G.A.O. and SALDANHA-CORRÊA, F.M.P. Influence of allochthonous organic matter on bacterioplankton biomass and activity in a eutrophic, sub-tropical estuary. *Estuarine, Coastal and Shelf Science*, 2009, 82(1), 84-94. http://dx.doi.org/10.1016/j.ecss.2008.12.020.

BORGES, A.C., SANDERS, C.J., SANTOS, H.L.R., ARARIPE, D.R., MACHADO, W. and PATCHINEELAM, S.R. Eutrophication history of Guanabara Bay (SE, Brazil) recorded by phosphorus flux to sediments from a degraded mangrove area. *Marine Pollution Bulletin*, 2009, 58(11), 1750-1765. PMid:19699494. http://dx.doi.org/10.1016/j.marpolbul.2009.07.025.

BORGES, A.V. and ABRIL, G. Carbon dioxide and methane dynamics in estuaries. In W. ERIC and M. DONALD, eds. *Treatise on estuarine and coastal science*. Amsterdam: Academic Press, 2011, pp. 119-161.

BOYES, S. and ELLIOTT, M. Organic matter and nutrient inputs to the Humber Estuary, England. *Marine Pollution Bulletin*, 2006, 53(1-4), 136-143.

PMid:16256145. http://dx.doi.org/10.1016/j.marpolbul.2005.09.011.

BRASIL. Conselho Nacional do Meio Ambiente – CONAMA. Resolução nº 357, de 18 de março de 2005. Dispõe sobre a classificação dos corpos de água e diretrizes ambientais para o seu enquadramento, bem como estabelece as condições e padrões de lançamento de efluentes, e dá outras providências. *Diário Oficial da União*, Poder Executivo, Brasília, DF, 18 mar. 2005.

BRASIL. Conselho Nacional do Meio Ambiente – CONAMA. Resolução nº 430, de 13 de maio de 2011. Dispõe sobre as condições e padrões de lançamento de efluentes, complementa e altera a Resolução no 357, de 17 de março de 2005, do Conselho Nacional do Meio Ambiente - CONAMA. *Diário Oficial da União*, Poder Executivo, Brasília, DF, 16 maio 2011.

BRICKER, S.B., FERREIRA, J.G. and SIMAS, T. An integrated methodology for assessment of estuarine trophic status. *Ecological Modelling*, 2003, 169(1), 39-60. http://dx.doi.org/10.1016/S0304-3800(03)00199-6.

BURTON, J.D. and LISS, P.S. *Estuarine chemistry*. London: Academic Press, 1976, 229 p.

CARREIRA, R.S. and WAGENER, A.L.R. Speciation of sewage derived phosphorus in coastal sediments from Rio de Janeiro, Brazil. *Marine Pollution Bulletin*, 1998, 36(10), 818-827. http://dx.doi.org/10.1016/S0025-326X(98)00062-9.

CONLEY, D.L., PAERL, H.W., HOWARTH, R.W., BOESCH, D.F., SEITZINGER, S.P., HAVENS, K.E., LANCELOT, C. and LIKENS, G.E. Controlling eutrophication: nitrogen and phosphorus. *Science*, 2009, 323(5917), 1014-1015. PMid:19229022. http://dx.doi.org/10.1126/science.1167755.

COTOVICZ JUNIOR, L.C., KNOPPERS, B.A., BRANDINI, N., COSTA SANTOS, S.J. and ABRIL, G. A strong CO2 sink enhanced by eutrophication in a tropical coastal embayment (Guanabara Bay, Rio de Janeiro, Brazil). *Biogeosciences*, 2015, 12, 6125-6146. http://dx.doi.org/10.5194/bg-12-6125-2015.

CRAPEZ, M.A.C., TOSTA, Z.T., BISPO, M.G.S. and PEREIRA, D.C. Acute and chonic impacts caused by aromatic hydrocarbons on bacterial communities at Boa Viagem and forte do Rio Branco beaches, Guanabara bay, Brazil. *Environmental Pollution*, 2000, 108(2), 291-295. PMid:15092959. http://dx.doi.org/10.1016/S0269-7491(99)00186-4.

DAY, J.W., HALL, A.S., KEMP, W.M. and YANEZ-ARANCIBIA, A. *Estuarine ecology*. New York: Wiley Interscience, 1989, 558 p.

DIAZ, R.J. and ROSENBERG, R. Spreading dead zones and consequences for marine ecosystems. *Science*, 2008, 321(5891), 926-929. PMid:18703733. http://dx.doi.org/10.1126/science.1156401.

EUROPEAN ENVIRONMENTAL AGENCY – EEA. *Nutrients in European ecosystems*. Luxembourg: Office for Official Publications of the European Communities, 1999, 155 p. Environental Assessment Report, vol. 4.

GOLTERMAN, H.L. and OUDE, N.T. Eutrophication of lakes, rivers and coastal seas. In O. HUTZINGER, ed. *The handbook of environmental chemistry*. Berlin: Springer Verlag, 1991, pp. 79-124.

GRASSHOFF, K., KREMLING, K. and EHRHARDT, M. *Methods of seawater analysis*. Weinheim: Verlag Chemie, 1999, 419 p.

GUIMARÃES, G.P. and MELLO, W.Z. Estimativa do fluxo de amônia na interface ar-mar na baía de Guanabara - estudo preliminar. *Quimica Nova*, 2006, 29(1), 54-60. http://dx.doi.org/10.1590/S0100-40422006000100012.

GUNDUZ, B., AYDIN, F., AYDIN, I. and HAMAMCI, C. Study of phosphorus distribution in coastal surface sediment by sequential extraction procedure (NE Mediterranean Sea, Antalya-Turkey). *Microchemical Journal*, 2011, 98(1), 72-76. http://dx.doi.org/10.1016/j.microc.2010.11.006.

HEAD, P.C. *Practical estuarine chemistry*. Cambridge: Cambridge University Press, 1985, 337 p.

INSTITUTO DE CONTROLE DO ESPAÇO AÉREO, MINISTÉRIO DA DEFESA COMANDO DA AERONÁUTICO – ICEA. *Dados Climatológicos: precipitação pluviométrica, temperatura do ar, velocidade e direção do vento à superfície e pressão (QNH). Aeroportos Santos Dumont (SBRJ) e Galeão Antônio Carlos Jobim (SBGL). Período: janeiro de 1951 a setembro de 2013*. 2013.

JAPAN INTERNATIONAL COOPERATION AGENCY – JICA. *The study on management and improvement of the environmental conditions of Guanabara bay of Rio de Janeiro, The Federative Republic of Brazil*. Rio de Janeiro: JICA and the State Secretariat of Environment and Urban Development, 2003, pp. 412.

KJERFVE, B., RIBEIRO, C.H.A., DIAS, G.T.M., FILIPPO, A.M. and QUARESMA, V.S. Oceanographic characteristics of an impacted coastal bay: baía de Guanabara, Rio de Janeiro, Brazil. *Continental Shelf Research*, 1997, 17(13), 1-13. http://dx.doi.org/10.1016/S0278-4343(97)00028-9.

KNOPPERS, B.A. and KJERFVE, B. Coastal lagoons of southeastern Brazil: physical and biogeochemical characteristics. In G. PERILLO, C. PICCOLO and M. PINO-QUIVIRA, eds. *Estuaries of South America*. Berlin: Springer, 1999, 223 p. http://dx.doi.org/10.1007/978-3-642-60131-6_3.

KNOPPERS, B.A., MEDEIROS, P.R.P., SOUZA, W.F.L. and JENNERJAHN, T. The São Francisco

Estuary, Brazil. In P. WANGERSKY, ed. *The handbook of environmental chemistry-water pollution: estuaries*. Berlin: Springer Verlag, 2006, pp. 51-70. http://dx.doi.org/10.1007/698_5_026.

LIBES, S.M. *An introduction to marine biogeochemistry*. New York: John Wiley & Sons, 1992, 734 p.

LISS, P. Conservative and non-conservative behavior of dissolved constituents during estuarine mixing. In J. BURTON and P. LISS, eds. *Estuarine chemistry*. New York: Academic Press, 1976, 255 p.

LUCAS, L.V., KOSEFF, F.R., CLOERN, J.E., MONISMITH, S.G. and THOMPSON, J.K. Processes governing phytoplankton blooms in estuaries. I: the local production-loss balance. *Marine Ecology Progress Series*, 1999, 197, 1-15. http://dx.doi.org/10.3354/meps187001.

MENICONI, M.F.G. *Baía de Guanabara: síntese do conhecimento ambiental***.** Rio de Janeiro: PETROBRAS, 2012, 337 p.

MORRIS, A.W. Estuarine chemistry and general survey strategy. In P.C. HEAD, ed. *Practical estuarine chemistry: a handbook***.** Cambridge: Cambridge University, 1985, 348 p.

MORRIS, A.W., BALE, A.J. and HOWLAND, R.J.M. Chemical variability in the Tamar Estuary, south-west England. *Estuarine, Coastal and Shelf Science*, 1982, 14(6), 649-662. http://dx.doi.org/10.1016/S0302-3524(82)80005-4.

NIXON, S.W. Remineralization and nutrient cycling in coastal marine ecosystems. In E. NEILSON and L. CRONIN, eds. *Estuaries and nutrients*. New Jersey: Human Press, 1981, pp. 111-138. http://dx.doi.org/10.1007/978-1-4612-5826-1_6.

NORIEGA, D.C., ARAUJO, M.C., TRAVASSOS, R.K. and NEUMANN-LEITÃO, S. Fluxos de nutrientes inorgânicos dissolvidos em um estuário tropical – Barra das Jangadas – PE, Brasil. *Tropical Oceanography*, 2005, 33(2), 133-145.

ODUM, E.P. and BARRET, G.W. *Fundamentos de Ecologia*. São Paulo: Cengage Learning, 2011, 612 p.

OLIVEIRA, E.N., FERNANDES, A.M., KAMPEL, M., CORDEIRO, R.C., BRANDINI, N., VINZON, S.B., GRASSI, R.M., PINTO, F., FILLIPO, A. and PARANHOS, R. Assessment of remotely sensed chlorophyll- a concentration in Guanabara Bay, Brazil. *Journal of Applied Remote Sensing*, 2016, 10(2), 1-20. http://dx.doi.org/10.1117/1.JRS.10.026003.

ORGANIZATION FOR ECONOMIC COOPERATION AND DEVELOPMENT – OECD. *Eutrophication of water: monitoring, assessment and control*. Paris: OECD, 1982, 154 p.

PAGLIOSA, P.R., FONSECA, A., BOSQUILHA, G.E., BRAGA, E.S. and BARBOSA, F.A.R. Phosphorus dynamics in water and sediments in urbanized and non-urbanized rivers in Southern Brazil. *Marine Pollution Bulletin*, 2005, 50(9), 965-974. PMid:15878601. http://dx.doi.org/10.1016/j.marpolbul.2005.04.005.

PARANHOS, R. and ANDRADE, L. Caracterização Físico-Química da coluna d'água e a qualidade das águas. In M.F.G. MENICONI, ed. *Baía de Guanabara: síntese do conhecimento ambiental*. Rio de Janeiro: PETROBRÁS, 2012, 337 p. vol. 1, Ambiente e influência antrópica.

PEREIRA, R.C. and GOMES, A.S. *Biologia Marinha*. Rio de Janeiro: Interciencia, 2002, 382 p.

PRITCHARD, D.W. and SCHUBEL, J.R. Physical and geological processes controlling nutrient levels in estuaries. In B.J. NEIL-SON and L.E. CRONIN, eds. *Estuaries and nutrients*. New York: Human Press, 1981, pp. 47-69. http://dx.doi.org/10.1007/978-1-4612-5826-1_3.

REDFIELD, A. The biological control of chemical factors in the environment. *American Scientist*, 1958, 46, 205-221.

REIS, J.A.T. and MENDONÇA, A.S.F. Análise técnica dos novos padrões brasileiros para amônia em efluentes e corpos d'água. *Engenharia Sanitária e Ambiental*, 2009, 14(3), 353-362. http://dx.doi.org/10.1590/S1413-41522009000300009.

RIBEIRO, C.H.A. and KJERFVE, B. Anthropogenic influence on the water quality in Guanabara Bay, Rio de Janeiro, Brazil. *Regional Environmental Change*, 2002, 3(1-3), 13-19. http://dx.doi.org/10.1007/s10113-001-0037-5.

RODRIGUES, R.P., KNOPPERS, B.A., SOUZA, W.F.L. and SANTOS, E.S. Suspended matter and nutrient gradients of a small-scale river plume in Sepetiba Bay, SE-Brazil. *Brazilian Archives of Biology and Technology*, 2009, 52(2), 503-512. http://dx.doi.org/10.1590/S1516-89132009000200030.

SANT'ANNA, E.B., CAMARGO, A.F.M. and BONOCCHI, K.S.L. Efeitos de descargas de esgotos domésticos na região estuarina da bacia do Rio Itanhaém (SP, Brasil). *Acta Limnologica Brasiliensia*, 2007, 19(2), 221-232.

SILVEIRA, R.P., RODRIGUES, A.P.C., SANTELLI, R.E., CORDEIRO, R.C. and BIDONE, E.D. Mass balance in the monitoring of pollutants in tidal rivers of the Guanabara Bay, Rio de Janeiro, Brazil. *Environmental Monitoring and Assessment*, 2011, 181(1-4), 165-173. PMid:21161585. http://dx.doi.org/10.1007/s10661-010-1821-9.

STRICKLAND, J.L.H. and PARSONS, T.R. *A practical handbook of seawater analysis*. Ottawa: Fisheries Research Board of Canada, 1972, 310 p.

TURNER, A. and MILLWARD, G.E. Particle dynamics and trace metal reactivity in estuarine plumes. *Estuarine, Coastal and Shelf Science*, 2000, 50(6), 761-774. http://dx.doi.org/10.1006/ecss.2000.0589.

TURNER, A. and MILLWARD, G.E. Suspended particles: their role in estuarine biogeochemical cycles. *Estuarine, Coastal and Shelf Science*, 2002, 45, 165-176.

VOLLENWEIDER, R.A. and KEREKES, J. *Eutrophication of waters: monitoring, assessment and control: report of OECD Cooperative Program on Eutrophication***.** Paris: Economic Development and co-Operation, 1982.

WINDOM, H.L., NIENCHESKI, L.F. and SMITH JUNIOR, R.G. Biogeochemistry of nutrients and trace metals in the estuarine region of the Patos Lagoon (Brazil). *Estuarine, Coastal and Shelf Science*, 1999, 48(1), 113-123. http://dx.doi.org/10.1006/ecss.1998.0410.

ZAR, J.H. *Biostatistical analysis*. 2nd ed. New Jersey: Prentice-Hall, 1999, 718 p.

ZHANG, R., WU, F., LIU, C., FU, P., LI, W., WANG, L., LIAO, H. and GUO, J. Characteristics of organic phosphorus fractions in different trophic sediments of lakes from the middle and lower reaches of Yangtze River region and Southwestern Plateau, China. *Environmental Pollution*, 2008, 152(2), 366-372. PMid:17698270. http://dx.doi.org/10.1016/j.envpol.2007.06.024.

Received: 13 May 2016
Accepted: 24 October 2016