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ASSESSMENT OF EUTROPHICATION THROUGH ECOLOGICAL INDICATORS AT THE ENTRANCE OF A TROPICAL URBANIZED ESTUARY

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ABSTRACT: Dissolved nutrients, phytoplankton biomass and other ancillary variables, were obtained at two sub-embayments at the entrance of Guanabara Bay (Rio de Janeiro, Brazil) and a composite trophic status index (TRIX) was used to assess the water quality of the study area. The role of bottom sediments in nutrient dynamics was also investigated through the evaluation nutrients, phytoplankton biomass and other sedimentary variables, since this compartment acts as a geological record of anthropogenic input. Jurujuba Sound, at the east margin, and Flamengo-Botafogo Sounds, at the western margin, were sampled during neap and spring tides in the dry season. Signs of eutrophication were detected through the extreme variations of dissolved oxygen concentrations at both margins, being more accentuated at Jurujuba Sound (2.20-14.07 mg.l^{-1}). Dissolved inorganic nitrogen was elevated at both margins and mostly composed of ammonium, surpassing 87% at Flamengo Botafogo Sounds, which suggests a continued input of raw sewage at the western margin of the bay. TRIX revealed poor water quality for most stations at the study area, varying from 4.53 to 7.29 at Jurujuba Sound and from 5.67 to 7.87 at Flamengo-Botafogo Sounds. The increase of TRIX from neap to spring tide was registered at both margins, revealing decrease of water quality. The differences in grain size between both margins played a key role in nutrient dynamics, with predominance of fine sediments at Jurujuba Sound and coarser particles at the opposite margin. Accumulation of high concentrations of TOC (0.87-6.57%) and inorganic phosphorus (154.34-1516.82 μg.g^{-1}) were favored by the predominance of fine sediments at Jurujuba Sound. The assessment of eutrophication in water column and bottom sediments revealed the maintenance of this process at the entrance of Guanabara Bay sustained by the recurrent anthropogenic input, what demands urgent action from public policies to mitigate this situation.

Keywords: nutrients, estuary, trophic index (TRIX), sediments.

RESUMO: *Nutrientes dissolvidos, biomassa fitoplanctônica, e outras variáveis auxiliares, foram obtidas em duas enseadas na estrada da Baía de Guanabara (Rio de Janeiro, Brazil) e um índice trófico composto (TRIX) foi utilizado para avaliar a qualidade da água na área de estudo. O papel dos sedimentos de fundo na dinâmica dos nutrientes também foi investigado através da avaliação de nutrientes, biomassa fitoplanctônica e outras variáveis sedimentares, já que este compartimento atua como um registro geológico de aporte antropogênico. A Enseada Jurujuba, na margem leste, e as Enseadas de Flamengo-Botafogo, na margem oeste, foram amostradas durante as marés de quadratura e sizígia na estação seca. Sinais de eutrofização foram detectados através da variação extrema de oxigênio dissolvido em ambas as margens, sendo mais acentuada na Enseada Jurujuba (2.20-14.07 mg.l^{-1}). O nitrogênio orgânico dissolvido foi elevado em ambas as margens e majoritariamente composto de amônio, ultrapassando 87% nas Enseadas Flamengo-Botafogo, o que sugeriu aporte contínuo de esgoto bruto na margem oeste da baía. O TRIX revelou baixa qualidade da água para a maioria das estações da área de estudo, variando de 4.53 a 7.29 na Enseada Jurujuba e de 5.67 a 7.87 nas Enseadas Flamengo-Botafogo. O aumento do TRIX entre quadratura e sizígia foi registrado em ambas as margens, revelando a piora da qualidade da água. As diferenças granulométricas entre ambas as margens tiveram papel fundamental na dinâmica dos nutrientes, com predominância de sedimentos finos na enseada Jurujuba e grãos mais grossos na margem oposta. A acumulação de elevada concentração de carbono orgânico total (TOC) (0.87-6.75%) e fósforo inorgânico (154.34-1516.82 μg.g^{-1}) foram favorecidos pela predominância de sedimentos finos na enseada Jurujuba. A avaliação da eutrofização na coluna d'água e sedimentos de fundo revelou a manutenção deste processo na entrada da Baía de Guanabara mantido pelo aporte antropogênico recorrente, o que demanda ação urgente do poder público para mitigar essa situação.*

Palavras-chave: *nutrientes, estuário, índice trófico, sedimentos.*

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1. INTRODUCTION

In the freshwater to ocean continuum, estuaries are crucial areas for the study of land-ocean interactions concerning marine biogeochemistry. Mixing of seawater and freshwater at ebb and flow tides in an hourly scale has a determinant role on nutrient dynamics as well as changes of physico-chemical properties. The extent of these effects is conditioned by tidal state and amplitude of coastal water (Anand *et al*., 2014; Barletta *et al*., 2019). The input of macronutrients in estuaries occurs naturally through riverine discharge and the understanding of their cycling depends on a series of factors including hydrodynamics, morphology, freshwater inflow and flushing time, microbial activity, particle and dissolved phases interactions and benthic exchanges. Apart from the aforementioned factors, the biogeochemistry of urbanized estuaries can also be influenced by anthropogenic input, leading to eutrophication, which can become a permanent condition and cause the degradation of the aquatic environment (Statham, 2012, Freeman *et al*., 2019).

Guanabara Bay has a long record of pollution of its waters and sediments, particularly discussing organic pollutants and trace metals, and the northwest portion of the bay is considered one of the most polluted areas of the estuary (Rebello *et al*., 1986; Machado *et al*., 2004; Farias *et al*., 2008; Borges *et al*., 2009; Aguiar *et al*., 2011; Abuchacra *et al*., 2015). Studies concerning macronutrients in the water column of Guanabara Bay are scarce (Aguiar *et al*., 2013; Abuchacra *et al*., 2015; Brandini *et al*., 2016; Guimarães and Mello, 2006; Júnior *et al*., 2006), especially concerning tidal variations. This estuary comprises harbors, oil and gas, fishing and tourism activities, and dredging of the harbor channel often takes place in this coastal area. The bay receives a heavy load of anthropogenic material mostly composed of raw sewage and industrial effluents. Approximately 50% of the urban households in the drainage basin of the bay are connected with sewage treatment stations, however, there has always been a deficit between produced and treated sewage, around 13%. The most recent estimation is that 18 $m^3.s^{-1}$ of untreated sewage is released into the bay (Coelho, 2007; Fistarol *et al*., 2015). With respect to macronutrients, the input of nitrogen and phosphorus into Guanabara Bay is estimated to be $6.2x10^{10}$ tonnes N/yr and $3.2x10^9$ tonnes P/yr, respectively, originated mostly from raw sewage (Wagener, 1995). Eutrophication is a condition often related in the inner portions of the bay (Soares-Gomes *et al*., 2016), associated with very elevated productivity and bottom hypoxia (Aguiar *et al*., 2011; Abuchacra *et al*., 2015; Brandini *et al*., 2016; Guenther and Valentin, 2008). Despite its huge economic importance to Brazil, the anthropogenic impact on Guanabara Bay is notorious and several attempts to reduce and control pollution have been discussed since 1994, when PDBG (Program for Remediation of Guanabara Bay) began through an international cooperation program between BID (Inter-American Development Bank) and JBIC (Japanese Bank for International Cooperation). New attempts to clean up the bay were discussed shortly before 2016 due to the fact that the city of Rio de Janeiro was chosen to host the Olympic Games in that year. However, very little results have been achieved with respect to cleaning up its waters, monitoring policies and sewage treatment, and Guanabara Bay continues to suffer the effects of huge loads of anthropogenic inputs.

The present study aims to assess pollution levels at the entrance of Guanabara Bay using a simple tool, a trophic index (TRIX) developed by Vollenweider *et al*. (1998) that is based on a linear combination of the log of four state variables (saturation of dissolved oxygen, chlorophyll-a, dissolved nitrogen and phosphorus), an approach that allows comparison with other urbanized coastal systems and widely used in eutrophication studies (Jayachandran and Nandan, 2012; Jungxiang *et al*., 2014; Brugnoli *et al*., 2019). Neap and spring differences were considered to check any significant differences between tidal flushes. Considering the fast dynamics of water column, especially in a semi-diurnal estuary, the assessment of eutrophication through sediment quality was also considered, since this compartment plays a key role as a geological record for the anthropogenic input. The northwest part of Guanabara Bay has always been considered a hot spot for pollution and this study attempts to show that the recurrent anthropogenic inputs also affect other parts of this estuary.

2. MATERIAL AND METHODS

2.1. Study Area

Guanabara Bay has an area of approximately 384 km^2 (Figure 1) with a drainage basin that has 4.080 km^2 and 45 rivers and channels, among which, six are responsible for approximately 85% of the total mean annual volume of freshwater discharged into the bay: Guapimirim, Iguaçu, Caceribu, Estrela, Meriti and Sarapuí (Coelho, 2007; Fistarol *et al*., 2015; Kjerfve *et al*., 1997).

Guanabara Bay is considered a mixed semidiurnal estuary with a microtidal range tidal range between 0.7 and 1.3 m.

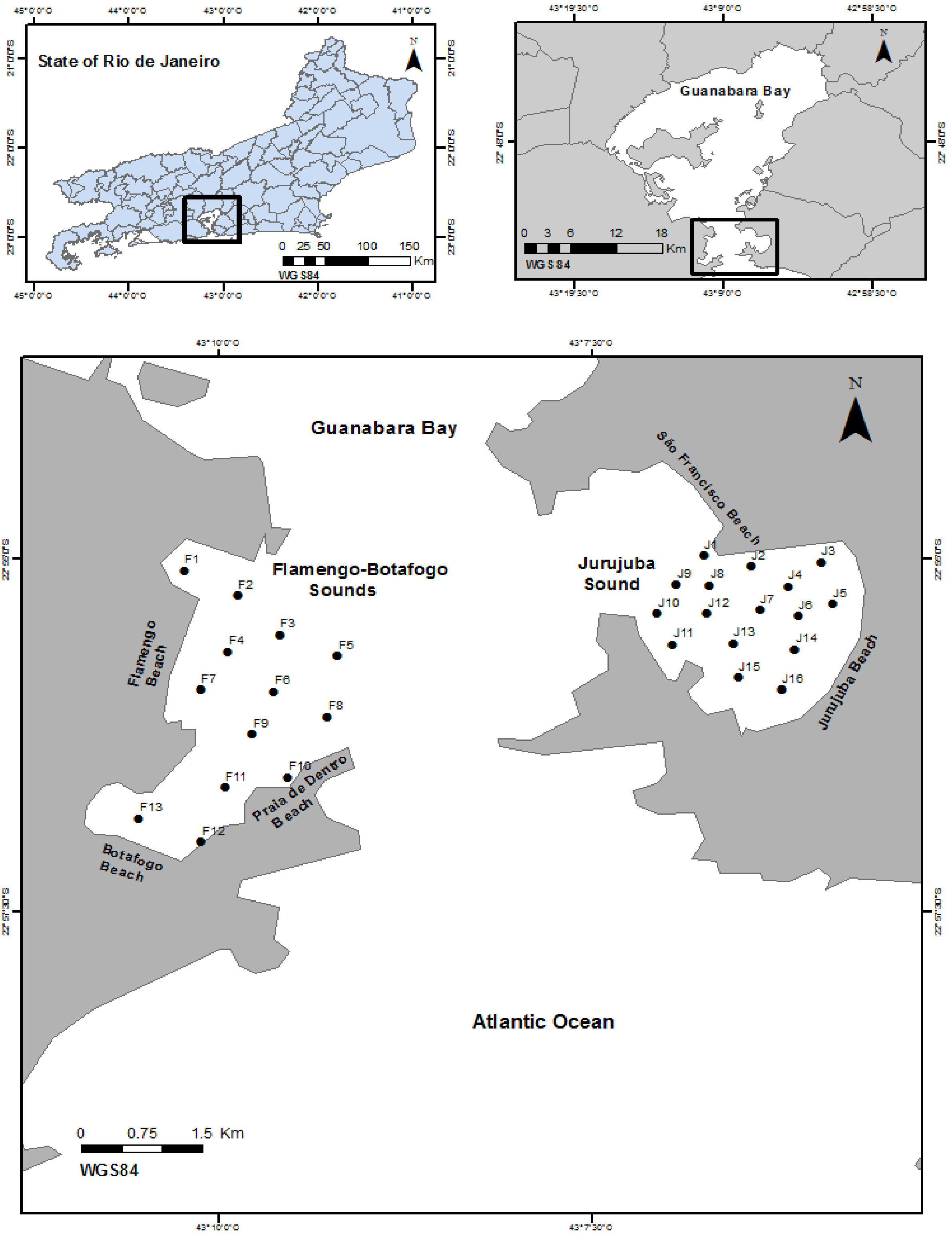

Figure 1. Study area and sampled stations.

The bay is tidally dominated, due to the predominance of shallow depths and slightly hypersynchronous, therefore the tidal range is greater at the landward margins than at the mouth of the bay. The input of fresh water into the bay is smaller than the inflow waters from the ocean, which means that fresh water inflow is not enough to affect the circulation pattern (Fries *et al.*, 2019). Circulation inside the bay is a composition of gravitational (bidirectional) and residual tide circulation, both affected by prevailing winds, and the time estimated to renew 50% of its waters is 11.4 days (Kjerfve *et al.*, 1997). The short residence time is not equal all around the bay; however, it prevents the water quality from getting worse in spite of the constant anthropogenic input. Sedimentation rates are high varying from 0.6 cm/year near the mouth to 4.5 cm/year in the inner part of the bay, and bottom sediments are composed of sand, muddy sand, sandy mud and mud (Amador, 1980; Kjerfve *et al.*, 1997; Soares-Gomes *et al.*, 2016).

The flux of anthropogenic input to Guanabara Bay is intense and constant, and dredging of the harbor area is frequent due to shipping and docking activities. Most of the watercourses in the drainage area are affected by high levels of pollutants, a consequence of domestic and industrial effluents from around 10.000 industries and 10 million population (Brandini *et al.*, 2016), characterizing Guanabara Bay as one of the most polluted coastal areas in Brazil. Within the cities situated at the northeast portion of the bay, around 48% of the sewage is collected. However, almost 97% of the collected sewage is discharged *in natura* into the bay. The situation around other parts of the bay is not better, and most of the sewage discharged into the bay is not treated at all. According to Soares-Gomes *et al.* (2016) previous environmental studies in Guanabara Bay, allow the identification of some pollution hot spots: (i) the area of Rio de Janeiro Harbor, mainly contaminated by trace metals and receiving the discharge of River Maracanã, one of the most polluted rivers of the drainage basin (Aguiar *et al.*, 2016; Cordeiro *et al.*, 2015); (ii) the northwestern area, where the main oil refinery is located and some of the most polluted rivers discharge (Estrela, Sarapuí, Meriti, Iguaçu); (iii) The eastern area in the proximities of the city of São Gonçalo and Niterói Harbor (Aguiar *et al.*, 2011; Neto *et al.*, 2005), considered the second biggest urban concentration of the metropolitan area; (iv) Jurujuba Sound, one of the most polluted sites (Abuchacra *et al.*, 2015; Baptista Neto *et al.*, 2000; Sabadini-Santos *et al.*, 2014).

2.2. Sampling and Analysis

Samplings occurred during the dry season of 2014, in July and August during daylight period. Jurujuba Sound and Flamengo-Botafogo Sounds were sampled twice during neap and spring tides each, therefore the data set corresponds to a total of four samplings. The tide range for neap and spring tides were between 0.5-0.9m and 0.0-1.2m, respectively. Water column was sampled near surface and bottom, in 16 stations at Jurujuba Sound and 13 at Flamengo-Botafogo Sounds (Figure 1). A multi probe YSI® 556 (Yellow Springs Instrument Company) was used to measure temperature, salinity, pH and dissolved oxygen (DO). Water samples were collected with a horizontal Van Dorn bottle and stored in polyethylene bottles pre-washed with HCl 10% (v/v) and rinsed with Milli-Q water. Bottles were immediately refrigerated in ice until arrival at laboratory. Bottom surface sediments were collected with a stainless steel Van Veen grab and samples were stored in plastic bags and immediately stored in ice.

At the laboratory water samples were filtered for determination of dissolved nutrients and suspended particulate material (SPM) with GF/F glass microfiber filters. Filtered samples for determination of dissolved inorganic phosphate (DIP) and dissolved inorganic nitrogen (DIN) were frozen at -20°C until the moment of analysis. After filtration GF/F membranes were used in the gravimetric determination of SPM according to Strickland and Parsons (1972). Determination of DIP and DIN was made through spectrophotometry as described in Grasshoff *et al.* (1999). Water samples were also filtered for the determination of chlorophyll-a (chlo-a) and phaeophytin-a (phae-a) with 0.45µm cellulose membranes which were frozen at -20°C in the dark for posterior analysis using 90% ketone extraction according to Strickland and Parsons (1972). Freeze-dried sediment samples were used for sediment analysis. Grain size analysis was performed through laser light scattering using a particle analyzer-Malvern series 2600, after elimination of organic matter and calcium carbonate with the method proposed by Suguio (1973). Total organic carbon (TOC) and total nitrogen (TN) were determined after elimination of carbonates with HCl 10% (v/v) in a Perkin Elmer Elemental Analyzer CHNS/O using acetanilide as a standard. Inorganic and organic phosphorus in sediments were determined following the method described in Aspila *et al.* (1976).

The software Statistica 7.0 was used to perform Mann Whitney test to evaluate significant differences for each sound between neap and spring tides and also between the sounds concerning the tides.

The Trophic Index (TRIX) initially proposed by Vollenweider *et al.* (1998) for costal marine areas is widely used in several coastal areas around the world. The index is a linear combination of four variables concerning nutritional factors and primary production and allows the comparison of different coastal areas concerning eutrophication. The calculation of TRIX uses concentrations of chlorophyll-a (mg.m^{-3}); oxygen as an absolute deviation from saturation D%O, TP-total phosphorus (mg.m^{-3}) and DIN-dissolved inorganic nitrogen (mg/m^3).

$$TRIX = \frac{1}{1.2}\,(log(Chla.|D\%O|.DIN.TP) - (-1.5))$$

The classification of coastal water by TRIX defines four categories of trophic state in terms of quality: (i) high, 2<TRIX<4; (ii) good- 4≤TRIX<5; (iii) moderate- 5≤TRIX<6 and (iv) poor- 6≤TRIX<8.

In the present study, TRIX was calculated for each station for surface and bottom waters.

3. RESULTS

3.1. Water column

Field work occurred in the dry season in the State of Rio de Janeiro in 2014. Precipitation during the sampling month was obtained from the meteorological station installed at Universidade Federal Fluminense (UFF) in Niterói-RJ and reached maximum values of 25 and 8 mm in July and August, respectively. Table 1 presents the ranges of variables registered in Jurujuba and Flamengo-Botafogo Sounds during neap and spring tides.

At Flamengo-Botafogo Sounds differences between neap and spring tides were significant for temperature (*p=0.00004*) and salinity (*p=0.00378*). Salinity varied between 25.90-27.69 and small stratifications were registered among the sampled stations during neap tide. During spring tide no haline stratifications were observed.

At Jurujuba Sound pH variation was higher during neap tide and was significantly different (*p=0.0000*) from spring tide (Tab. 1). At Flamengo-Botafogo Sounds, pH values were typical for marine waters, varying from 8.05 to 8.64 and from 8.28 to 8.55 during neap and spring tides, respectively.

Dissolved oxygen at Jurujuba Sound varied between 4.51-14.07 mg.l^{-1} and 2.20-10.73 mg.l^{-1} in neap and spring tides, respectively, with significant differences between them (*p=0.00001*). During spring tide, with the exception of J10, every station at Jurujuba Sound presented DO values below 5 mg.l^{-1}, at bottom waters, characterizing poor oxygenation and reaching saturation levels as low as 38%. Some stations presented DO levels under 5.00 mg.l^{-1} at surface and bottom waters (J11, J14 and J16). The lowest DO concentration was registered at bottom water of J3, 2.20 mg.l^{-1}.

Concentrations of DO at Flamengo-Botafogo Sounds were low during neap tide, maintaining saturation values under 80% and reaching values as low as 41.51% at F1, in the marina area. With tidal change, water oxygenation improved significantly (p=0.00116) during spring tide, with only a few inner stations (F1, F12 and F13) presenting DO<5.00 mg.l^{-1}. Saturation of the water column was around 80% for most stations, however, values as low as 38.47% were registered during spring tide, close to Botafogo Beach (F13). The marina area (F1) also presented a low saturation value, 53%.

Table 1. Neap-spring variations of depth (m), temperature (oC), salinity, pH, dissolved oxygen (mg.l^{-1}), saturation of dissolved oxygen (%), chlorophyll-*a* (µg.l^{-1}), phaeophytin-*a* (µg.l^{-1}), dissolved inorganic phosphorus (µM) and dissolved inorganic nitrogen (µM) at Jurujuba and Flamengo-Botafogo Sounds

Tide		Depth (m)	T	S	pH	DO	%DO	Chl-a	Phae-a	DIP	DIN
						Jurujuba Sound					
Neap	Min	2.5	22.72	27.11	7.31	4.51	11.60	0	0	0.05	1.11
	Max	6.0	23.71	28.44	8.97	14.07	207.30	24.72	126.56	0.71	7.43
Spring	Min	2.0	22.33	27.34	7.48	2.20	33.90	0.59	0.06-	0.22	1.02-
	Max	6.1	23.79	28.65	7.89	10.73	167.30	32.04	43.65	1.09	5.63
						Flamengo-Botafogo Sounds					
Neap	Min	6.7	19.80	20.44	8.05	3.00	41.51	0.36	0.21	0.33	2.92
	Max	19.0	20.80	28.76	8.64	5.18	71.26	7.12	11.84	1.73	28.79
Spring	Min	4.0	20.68	25.90	8.28	2.78	38.47	0	1.09	1.16	7.52
	Max	30.0	23.30	27.59	8.55	6.11	88.61	45.39	74.83	4.63	48.52

Phytoplankton biomass at Jurujuba Sound was low at most stations during neap tide, varying from zero to 24.72 $\mu g.l^{-1}$, whereas phaeophytin-*a* varied between zero and 126.56 $\mu g.l^{-1}$. During spring tide chlorophyll-*a* peaked at Jurujuba Sound and reached the highest value at surface water of J4 (32.04 $\mu g.l^{-1}$). Other peaks of chlorophyll-*a* were also registered during spring tide at surface waters of J1, J3, J8 and J9 with values between 9.49 and 26.11 $\mu g.l^{-1}$. Neap-spring tide differences were significant (*p=0.026946*), and concentrations of chlorophyll-*a* were lower during neap tide.

At Flamengo-Botafogo Sounds, concentrations of chorophyll-*a* during spring tide were significantly different from neap tide (*p=0.000627*), since phytoplankton biomass was only detected at some inner stations F7, F11, F12 and F13. The elevated chlorophyll-*a* concentration found at F13 at surface and bottom waters (35.04-45.39 $\mu g.l^{-1}$), suggested a local phytoplankton bloom at Botafogo Beach. Phaeophytin-*a*, on the other hand, was detected in every station, during spring tide, with the exception of F13, revealing a massive presence of degraded phytoplankton biomass. During spring tide, concentrations of phaeophytin-*a* were significantly different from neap tide (*p=0.001235*) and ranged from 1.09 $\mu g.l^{-1}$ (F12) to 74.83 $\mu g.l^{-1}$ (F6).

Dissolved inorganic phosphorus presented significant differences (*p=0.00001*) between neap and spring tides at Jurujuba Sound. Higher concentrations of DIP (>0.70μM) were registered during spring tide at stations J11-J16, closer to a marina area. At Flamengo-Botafogo Sounds concentrations of DIP during neap tide varied from 0.33 to 1.73μM, with higher values at the inner stations F1, F12, F13 and also at F3 and F5. During spring tide, DIP concentrations increased significantly (*p=0.00001*), varying from 1.16 to 4.63 μM, and higher concentrations were registered again at F1, located at the marina area in Flamengo, F12 and F13, at Botafogo beach, and F10, close to Praia de Dentro.

DIN did not present significant differences between neap and spring tides (*p=0.428238*) at Jurujuba Sound. During neap tide, the percentage of ammonium in DIN was between 37 and 99%. With change to spring tide, ammonium was not detected at several stations (J7, J10, J11, J12, J13, J14, J15) and its fraction in DIN varied between 1 and 58%. DIN varied significantly between neap and spring tides (*p=0.000963*) at Flamengo-Botafogo Sounds. The highest fraction of DIN at Flamengo-Botafogo Sounds was composed of N-NH4 during neap (87-97%) and spring (88-98%) tides.

During neap tide, with the exception of salinity and chlorophyll-*a*, all the variables were significantly different between Jurujuba and Flamengo-Botafogo Sounds (Tab. 2). In spring tide, differences between both margins at the entrance of the bay were also considered significant for most variables, except for dissolved oxygen, saturation of DO and chlorophyll-*a*.

Table 2. Mann-Whitney analysis (p<0.05) between Jurujuba and Flamengo-Botafogo Sounds for neap and spring tides.

Variables	Neap tide *p*	Spring tide *p*
Temperature	0.000000	0.000000
Salinity	0.266958	0.000000
pH	0.000000	0.000000
DO	0.000000	0.139812
%sat DO	0.000000	0.777842
Chl-*a*	0.669816	0.011669
Phae-*a*	0.000001	0.000083
DIN	0.000001	0.000000
DIP	0.000000	0.000000

3.2. Sediments

Bottom sediments at Jurujuba Sound exhibited predominance of pelitic sediments, with concentrations of silt and clay over 50%. Stations J3, J5, J7 did not reach 50% of silt and clay, but surpassed 40%, and J16 presented less than 10% of silt and clay. At Flamengo-Botafogo Sounds grain size analysis revealed the predominance of sandy sediments at the bottom of the sounds (Figure 2).

The total content of calcium carbonate at Jurujuba Sound (Figure 2) varied between 3.80 to 43.38% (Figure 2) and results classified stations J6-J14 as litobioclastics (>30%) whereas the rest of them was classified as litoclastic (Larssouner *et al*., 1982). On the other side of the bay, Flamengo-Botafogo Sounds presented carbonate contents that classified bottom sediments as litoclastics, with the exception of F11, with more than 40% of $CaCO_3$ (litobioclastic).

At Flamengo-Botafogo Sounds TOC contents were low, mostly under 0.5%, except for F4 and F11, with 3 and 8.26%, respectively (Figure 2). Contrasting results of TOC were found at Jurujuba Sound, with most concentrations elevated between 0.87 and 6.57% (Figure 2).

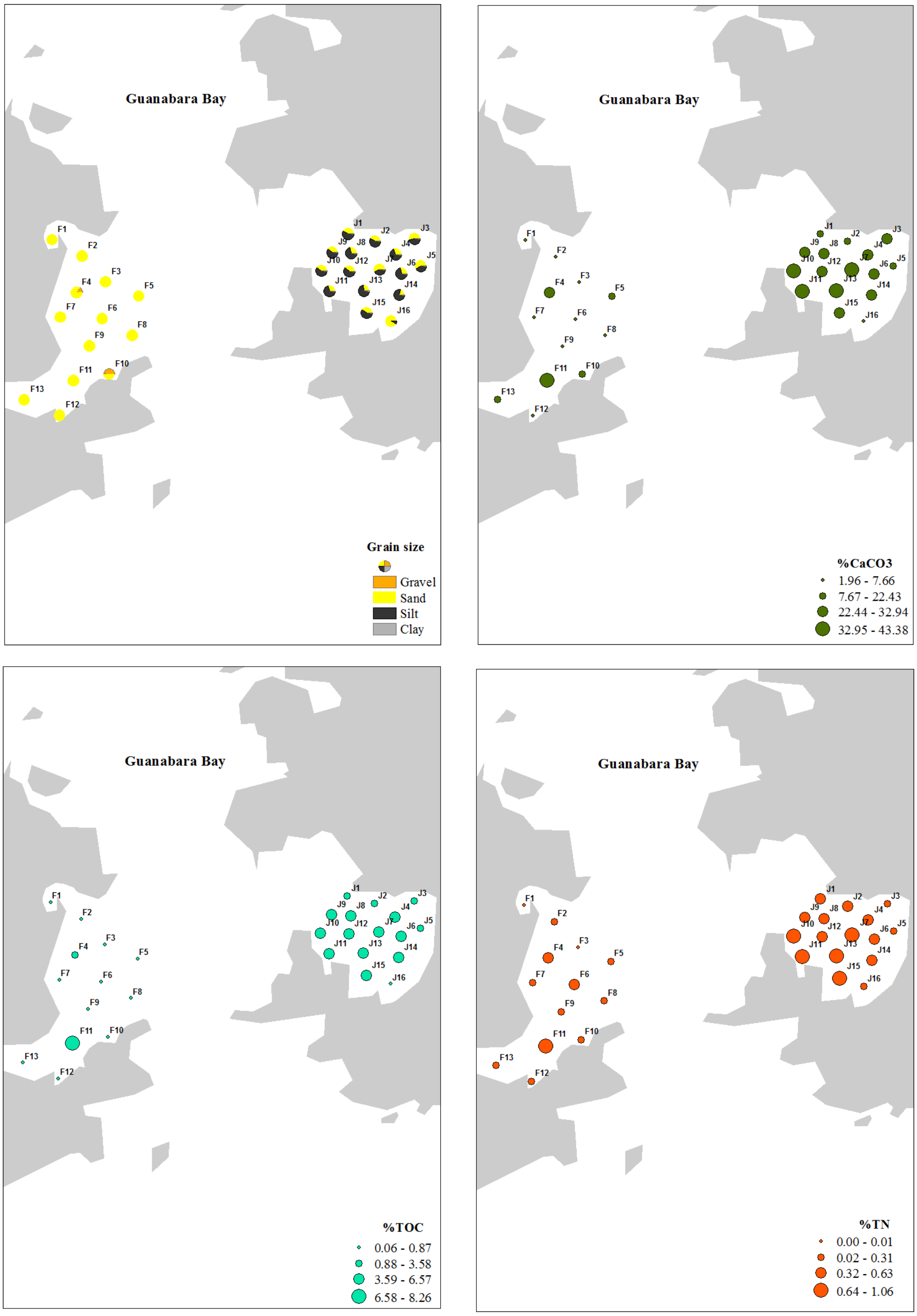

Figure 2. Grain size, calcium carbonate ($CaCO_3$), total organic carbon (TOC), total nitrogen (TN) for bottom sediments at Jurujuba and Flamengo-Botafogo Sounds.

Chorophyll-*a* was not detected in the sediments of Jurujuba Sound (Figure 3), except for J16 with a low value, 0.67 $\mu g.g^{-1}$, whereas phaeophytin-*a* was registered in every station, varying from 6.85 to 34.12$\mu.g^{-1}$. Chlorophyll-*a* was detected only at a few stations in Flamengo-Botafogo Sounds and the highest concentration was registered at F11, 1.47 $\mu g.g^{-1}$ (Figure 3). Results of chlorophyll-*a* and phaeophytin-*a* suggest the predominance of degradation process at both sub-embayments (Figure 3).

Concentrations of inorganic phosphorus (IP) at bottom sediments at Jurujuba Sound presented a range (Figure 3), from 154.34 (J16) to 1516.82 $\mu g.g^{-1}$ (J9). The concentrations of organic phosphorus at Jurujuba Sound, were markedly smaller than the inorganic form, varying from 20.34 to 965.61 $\mu g.g^{-1}$ (Figure 3). In contrast to the opposite margin, the accumulation of phosphorus on Flamengo and Botafogo Sounds was predominantly under the organic form. Concentrations of IP were mostly under 600 $\mu g.g^{-1}$, varying between 69.80 to 1699.63 $\mu g.g^{-1}$. whereas organic phosphorus varied from 2.45 to 20.232.14 $\mu g.g^{-1}$ (Figure 3).

Differences between the two sub-embayments at the entrance of Guanabara Bay were considered significant for the sediment variables, with the exception of chlorophyll-*a* and gravel (Table 3).

Table 3. Mann-Whitney analysis ($p<0.05$) for bottom sediment variables between Jurujuba and Flamengo-Botafogo Sounds.

Variables	*p*
IP	0.000702
OP	0.043053
$CaCO_3$	0.001006
TOC	0.000193
TN	0.003302
Chl-*a*	0.160531
Phae-*a*	0.000055
gravel	0.982507
sand	0.000014
silt	0.000005
clay	0.000005

4. DISCUSSION

4.1. Water column

Results proved to be significant differences of anthropogenic inputs and nutrient dynamics between the two opposite margins at the entrance of Guanabara bay. Depth variations between the two sub-embayments can account for marked differences concerning some physical variables. Smaller temperature ranges at Jurujuba Sound during both tidal periods, can be justified by it shallowness (up to 6 m) and darker waters favoring higher temperatures, whereas at Flamengo-Botafogo Sounds depths can reach more than 20 m. Fries *et al*. (2019) described that water column at the entrance of the bay is well mixed, and this mixed water reaches up to 15-20 km inside the bay, with current velocities around 0.5 $m.s^{-1}$ in deeper areas, reducing to approximately 0.1 $m.s^{-1}$ in shallower depths. According to Kjerfve *et al*. (1997), haline stratifications at Guanabara Bay are weak or moderate never exceeding 4 salinity units. Indeed, this was the case of Flamengo-Botafogo Sounds during neap tide, with differences between surface and bottom waters up to 2 units, except for F1 where differences in salinity from top to bottom reached 6 units. Station F1 is an inner one located in a marina area; therefore, this stratification could probably be caused by anthropogenic discharge in this area.

Concentrations of DO below 5.00 $mg.l^{-1}$ are the beginning of biological stress for many aquatic species with lower tolerance to anoxic conditions, especially the ones in higher levels of the food chain (Bricker *et al*., 2003; Kadiri *et al*., 2014). Moreover, hypoxia/anoxia conditions can also be reached during the night period, due to predominance of respiration and decomposition processes and excess of organic matter. Hypoxia is a matter of concern when it comes to Jurujuba Sound in particular since it comprises local fishing communities and mariculture. Previous studies have detected hypoxia at Jurujuba Sound (Aguiar *et al*., 2013; Abuchacra *et al*., 2015), with values as low as 0.86 $mg.l^{-1}$ at bottom waters. Despite the fact that low concentrations of DO were observed at both sub-embayments, concentrations did not characterize hypoxia during sampling, that occurred during daylight. The differences in the levels of dissolved oxygen between the two margins were highlighted, especially during neap tide (Figure 4). The degradation of excess organic matter drives the consumption of dissolved oxygen, which was mainly observed at waters adjacent to bottom sediments, with DO levels $<5.00\ mg.l^{-1}$. In the case of Jurujuba Sound, lower concentrations of DO were accompanied by lower pH values, especially during spring tide, corroborating the hypothesis of mineralization of organic matter. Higher values of DO during neap tide were also accompanied by higher pH values, suggesting intense primary production at Jurujuba Sound (Figure 4).

At Flamengo-Botafogo Sounds, the levels of DO slightly increased from neap to spring tide, except for the most inner stations F1 and F13 which maintained low concentrations of dissolved oxygen.

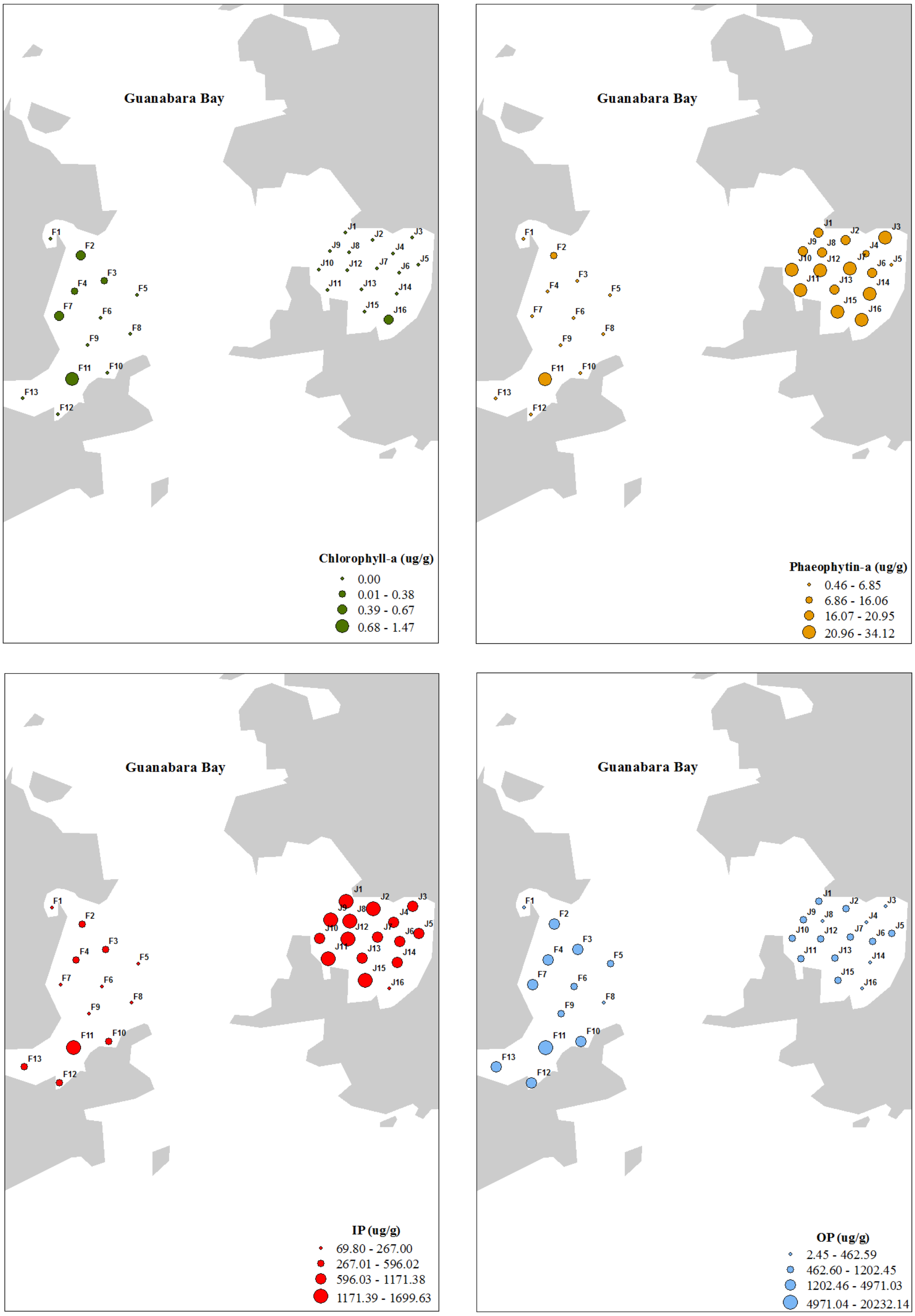

Figure 3. Chlorophyll-*a*, phaeophytin-*a*, inorganic phosphorus (IP) and organic phosphorus (OP) at bottom sediments from Jurujuba and Flamengo-Botafogo Sounds.

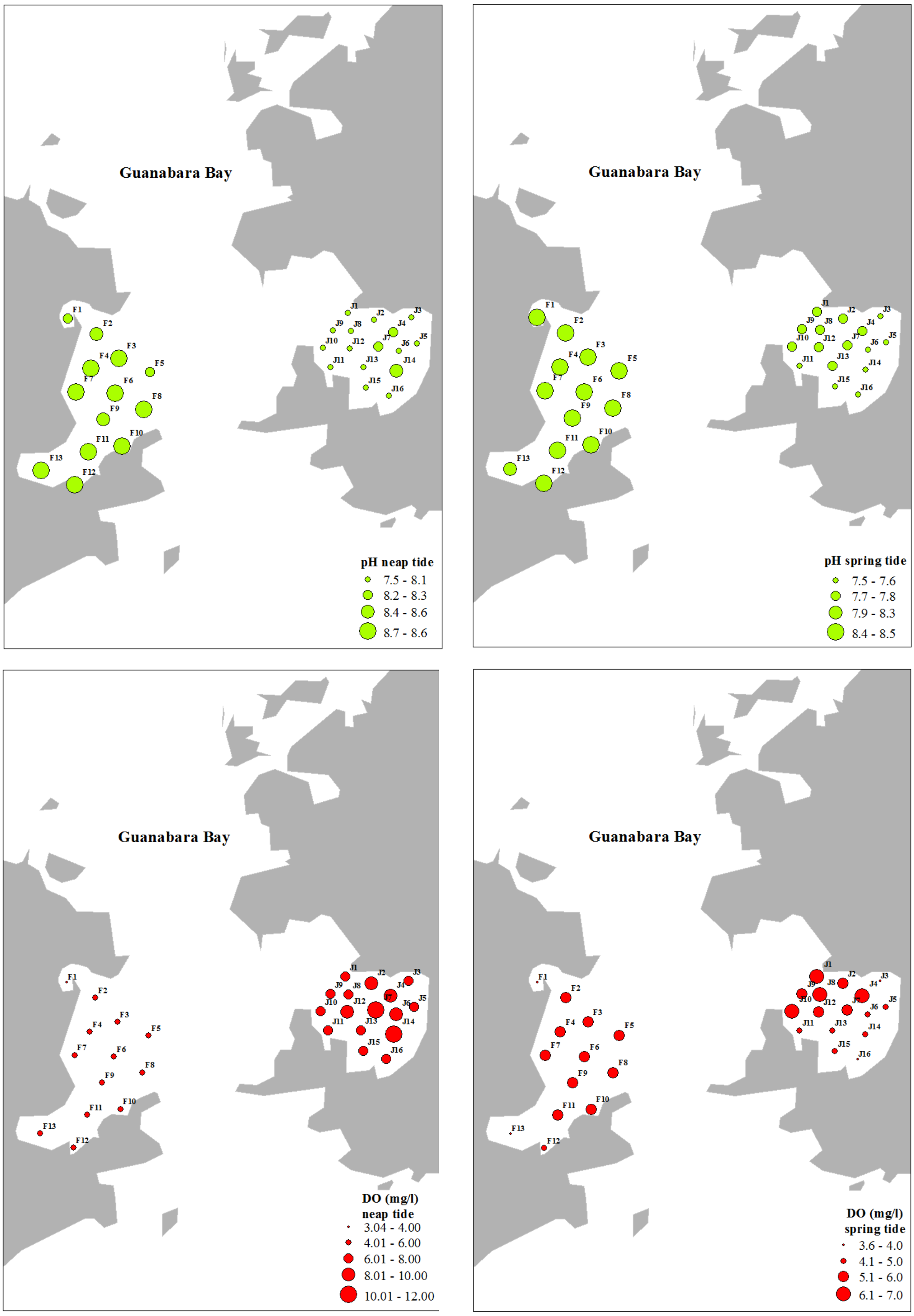

Figure 4. Mean values (surface and bottom) for pH and dissolved oxygen (DO) at Jurujuba and Flamengo-Botafogo Sounds during neap and spring tides.

This is probably caused by the restricted circulation at these areas, as well as smaller depth and the input of fresh water and sewage at these locations. The main fluvial influences at the study area are the Berquó and Banana Podre rivers, both channeled. These rivers receive municipal untreated wastewater and converge before reaching Botafogo Sound (F13). Station F1, on the other hand is located inside Marina da Glória under the direct influence of sewage input, presenting strong septic smell and dark waters.

The differences in the contents of phytoplankton biomass between the opposite margins were also striking, with chlorophyll-*a* concentrations clearly higher at Jurujuba Sound (Figure 5). The peaks of chlorophyll-*a* were consistent with concentrations of DO higher than 5 $mg.l^{-1}$ during spring tide (J1, J3, J8, J9), suggesting predominance of production processes, which was corroborated by chlorophyll-*a*/phaeophetyin-*a*>1 at these sites. However, at most stations during spring tide, chlorophyll-*a*/phaeophytin-*a* was <1, in accordance with low values of DO and pH, suggesting the occurrence of degradation processes. Only at F7, F11 and F12 chlorophyll-*a* and phaeophytin-*a* were both detected in spring tide with a ratio chlorophyll-*a*/phaeophytin-*a* >1, pointing to production at these stations.

Concentrations of dissolved inorganic phosphorus were significant different between the two margins, and lower concentrations of DIP at Jurujuba Sound (Figure 6) may be attributed to sorption processes of phosphorus on fine sediments. At Flamengo-Botafogo Sounds, on the other hand, the sorption of phosphorus by bottom sediments is lessened by the predominance of coarser particles at the bottom. Ammonium is usually the most abundant form of nitrogen in surface waters after phytoplankton blooms remove most of nitrate and phosphate, and is also excreted by organisms along with urea and peptides. The decrease in DIN concentrations, including ammonium, at Jurujuba Sound in spring tide coincided with the peaks of chlorophyll-*a*, suggesting that phytoplankton could have alternatively assimilated $N\text{-}NH_4^+$ for primary production which has a lower energetic cost for cells associated with protein synthesis (Parker *et al*., 2012).

High percentages of ammonium in DIN composition can also be originated from anthropogenic input of raw sewage, through the hydrolysis of urea, and decomposition of other nitrogen organic compounds. During both tides, peaks of DIN with high concentrations of $N\text{-}NH_4^+$, occurred at stations F7 and F9, in front of Flamengo Beach and also at F12 close to Botafogo Beach. This confirms a continuous input at this location, probably trough domestic effluents which are maintained in the water column for a longer time due to restricted circulation patterns of the area. The increase in DIN at most stations during spring tide was accompanied by the depletion of phytoplankton biomass at most stations. Some studies relate inhibition of primary production due to excess $N\text{-}NH_4^+$. The increase of nutrients drives eutrophication, however, high concentrations of chlorophyll-*a* are only achieved once the larger dissolved inorganic nitrogen pool is accessed.

Concentrations of ammonium above a threshold value may inhibit the assimilation of NO_3^-. Dugdale *et al*. (2007) and Dugdale *et al*. (2012) described concentrations of ammonium above 4μM as inhibitory by for assimilation of nitrate by phytoplankton for primary production in a study at San Francisco estuary. Overall concentrations of $N\text{-}NH_4^+$ were elevated during both tides at Flamengo-Botafogo Sounds, higher than 4μM, which may justify the low concentrations of chlorophyll-*a* especially in spring tide. It is therefore, reasonable to infer that DIN with ammonium concentrations under 4μM at Jurujuba could be used to enhance primary production, whereas the excess of this nutrient would inhibit primary production at Flamengo-Botafogo Sounds.

Table 4 compares concentrations of DIP, DIN, DO and chlorophyll-*a* from the present study with past ones at Guanabara Bay. Except for Fistarol *et al*. (2015), who presented data from the entrance of the Guanabara Bay, results from past studies were obtained from different locations inside the bay. Overall, results obtained in the present study fell within the range registered in previous studies at Guanabara Bay, revealing a continuous anthropogenic impact of its waters over the last decades.

4.2. Trophic index (TRIX)

Figure 7 shows results of trophic index (mean±SE) at the entrance of Guanabara Bay. Overall, TRIX values did not present a wide range of throphic conditions, revealing a mostly degraded environment at both sub-embayments, varying from good (4≤TRIX<5) to poor (6≤TRIX<8).

At Jurujuba Sound the increase of TRIX from neap to spring tide was clear in every station. During neap tide, water condition of over 50% of the stations was considered good, and the rest of them moderate. With tidal change, water quality decreased to poor condition at most stations. At Flamengo-Botafogo Sounds, the calculation of TRIX was not possible at some stations, mostly for spring tide, since chlorophyll-*a* was not detected at several stations. Despite the fact that water quality at Flamengo-Botafogo Sounds was already considered poor at most stations, it was noticeable that TRIX also increased from neap to spring tide, and the stations classified with moderate

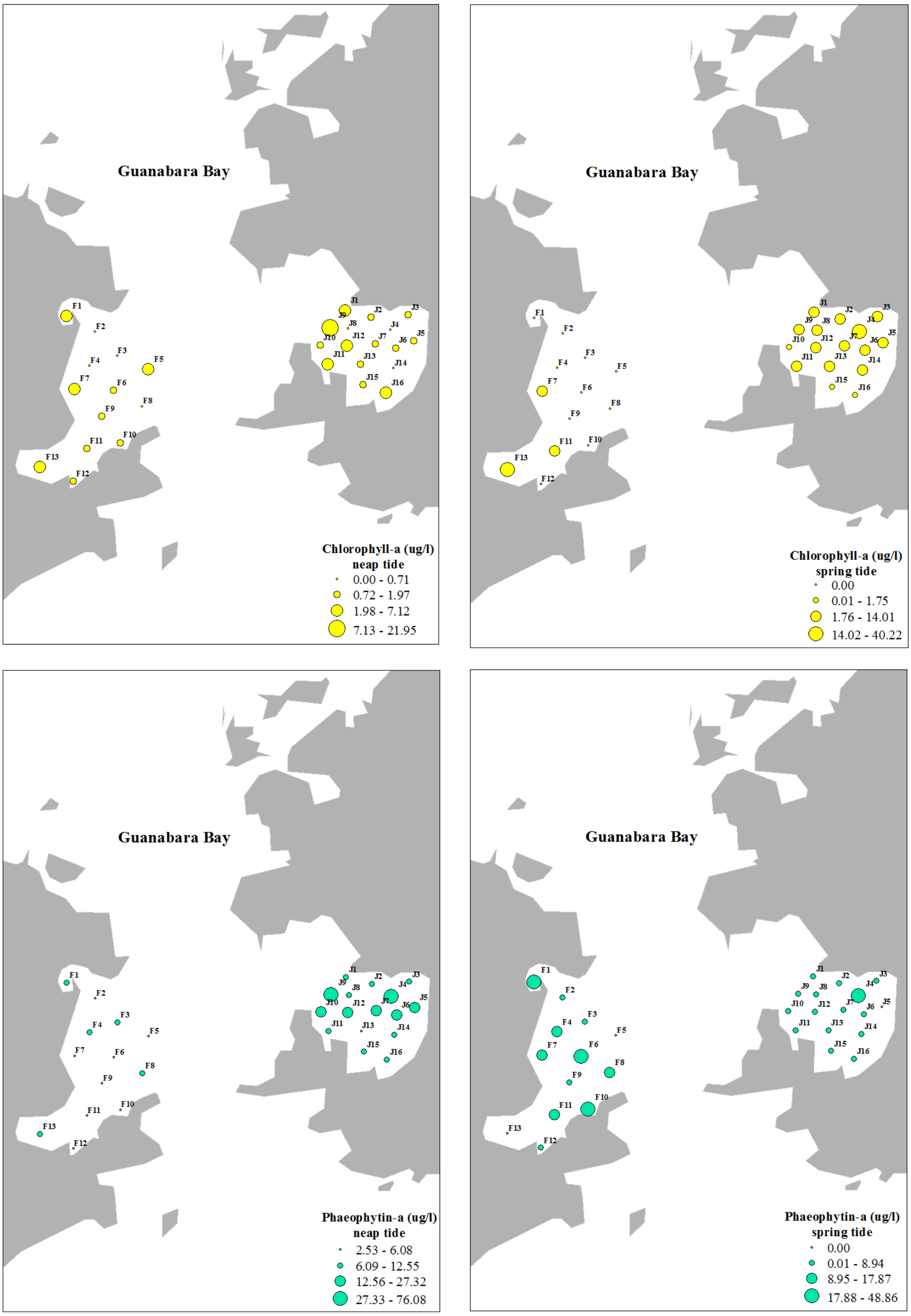

Figure 5. Mean values (surface and bottom) for cholophyll-a and phaeophytin-a at Jurujuba and Flamengo-Botafogo Sounds during neap and spring tides.

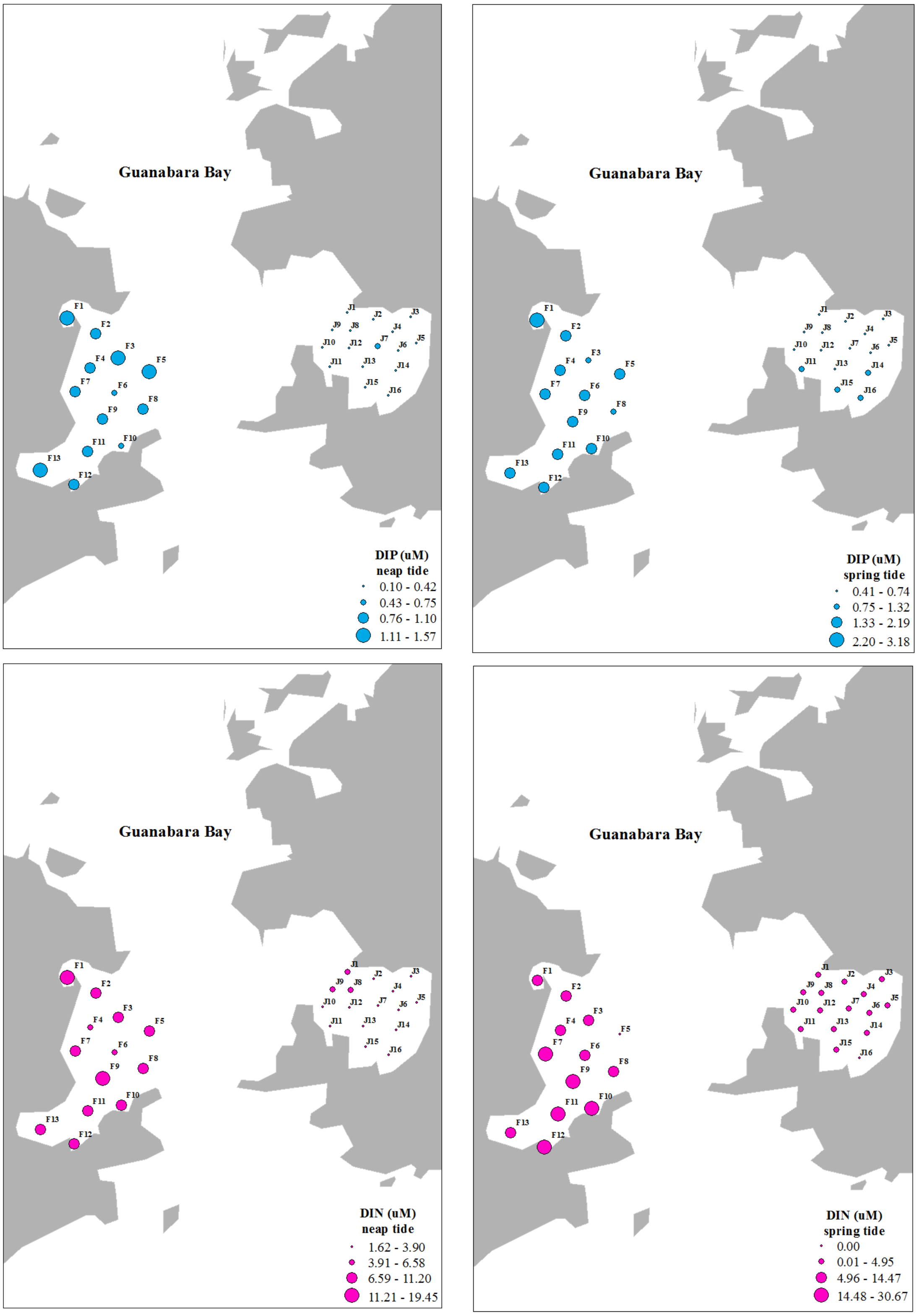

Figure 6. Mean values (surface and bottom) for dissolved inorganic phosphorus (DIP) and dissolved inorganic nitrogen (DIN) at Jurujuba and Flamengo-Botafogo Sounds during spring tide.

Table 4. Concentrations of dissolved inorganic phosphorus (DIP), dissolved inorganic nitrogen (DIN) chlorophyll-*a* (Chl-*a*) and dissolved oxygen (DO) in the water column, from past studies at Guanabara Bay and the present one.

Study	**DIP (µM)**	**DIN (µM)**	**Chl-*a* (µg.l-1)**	**DO (mg.l-1)**
*Kjerfve *et al*. (1997)	0.003-0.12	0.13-7.07	20.6-102.7	3.1-11.1
Gonzalez *et al*. (2000)	0.86	10.36	26.03	6.1
*Fistarol *et al*. (2015)	0.05-7-4	0.60-68.3	0.5-8.2	0.28-3.97
*Brandini *et al*. (2016)	3.4	124	82.8	9.1
This study, Flamengo-Botafogo Sounds	0.33-4.63	2.92-48.52	0.36-45.39	2.78-6.11
This study, Jurujuba Sound	0.05-1.09	1.02-5.63	0.59-32.40	2.20-14.07

*mean values

water quality decreased to poor. The shift from neap to spring tide seemed to decrease water quality at the entrance of Guanabara Bay. One of the main factors that could decrease water quality at Guanabara Bay is fluvial discharge, however, no significant differences in precipitation were registered between sampling periods to affect anthropogenic input at the sounds. The fluctuations of flood and ebb tide during sampling certainly influences TRIX since Guanabara Bay is a semi-diurnal estuary and biogeochemical processes in the water column are very dynamic. Nevertheless, most of the stations were sampled during flood tide. The index is quite sensitive and even little fluctuations of nutrients, chlorophyll-*a* or dissolved oxygen are enough to shift water quality. Raw data proved that there was indeed an increase in the variables used for TRIX calculations from neap to spring tide at Flamengo-Botafogo Sounds (Figure 5 and Figure 6). For Jurujuba Sound, the increase of DIP and chlorophyll-*a* from neap to spring tide was enough to decrease water quality. According to Fries *et al*. (2019), the ocean waters from beaches located outside Guanabara Bay, like Copacabana and Ipanema, can enter the bay during flood tide. This entrained water brings along the untreated sewage from the Ipanema marine outfall, which certainly affects the water quality at the entrance of the Bay. TRIX results for Guanabara Bay were close to the values of impacted coastal areas, such as Mediterranean Ecoregion and Youngsan River at South Korea (Tab. 5) and presented the highest values among them.

4.3. Bottom sediments

Results of the present study concerning bottom sediments show that they play a crucial role in biogeochemistry at the entrance of the bay. The accumulation of high concentrations of organic matter at Jurujuba Sound bottom sediments is favored by its small depths and predominance of fine sediments. TOC results at Jurujuba Sound were higher than the results obtained by and by Baptista Neto *et al*. (2000) (TOC<5%) and Abuchacra *et al*. (2015) in the same area (TOC<5.06%), suggesting the increase of anthropogenic input at the east margin in the past years. In a study conducted in six eutrophic estuaries at north-eastern Brazil, Silva *et al*. (2017), found average TOC values between 0.42 and 2.69%, much lower than the ones found in the present study, suggesting a high anthropogenic pressure at the entrance of Guanabara Bay, especially at Jurujuba Sound.

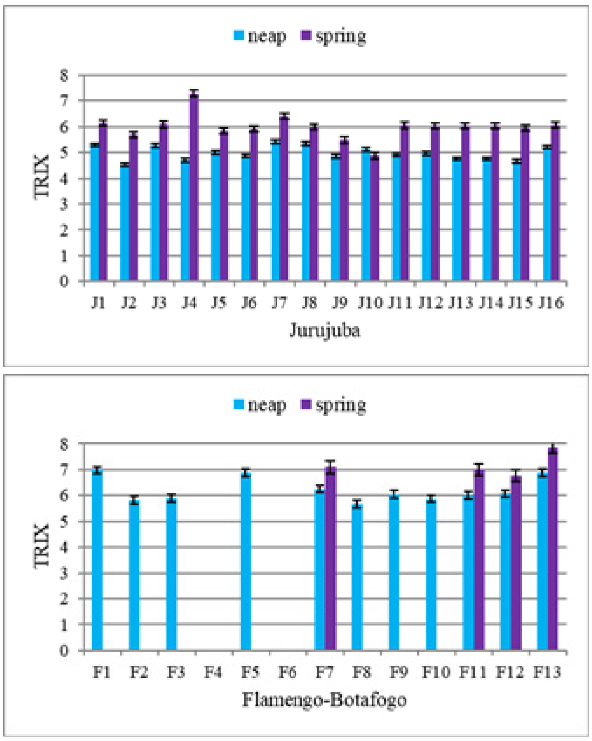

Figure 7. Mean values of trophic index (TRIX) calculated for Jurujuba and Flamengo-Botafogo Sounds, for neap and spring tides.

Table 5. Trophic Index (TRIX) calculated according to Vollenweider *et al.* (1998) for different coastal areas.

	TRIX
Mediterranean Ecoregion, Italy (Pettine *et al*., 2007)	2.99-6.03
Gulf of Riga, Baltic coast (Boikova *et al*., 2008)	3.48-5.83
Coastal area of Sicily, Italy (Caruso *et al*., 2010)	0.99-6.02
Youngsan River Estuary- Korea (Sin *et al*., 2013)	5.9-6.5
Portuguese Continental Exclusive Economic Zone (Cabrita *et al*., 2015)	4.2-6.3
Eastern Mediterranean (Simboura *et al*., 2016)	1.31-6.02
This study, Jurujuba Sound	4.53-7.29
This study, Flamengo-Botafogo Sounds	5.67-7.87

At both sub-embayments, anthropogenic inputs of nutrients enhance the production of organic matter as shown by the results of C/N ratios. At Jurujuba Sound, organic matter OM was considered of mixed origin tending to marine ($8.1<C/N<9.7$) (Bader, 1955). At Flamengo Botafogo Sounds, $C/N<6$ for most stations revealed OM of marine origin. The exceptions were F2 and F11 with OM classified as mixed origin tending to marine ($6<C/N<12$). Results at Flamengo-Botafogo Sounds were higher than the ones found by Eichler *et al*. (2003) ($TOC<4.6\%$) for Guanabara Bay.

Elevated concentrations of chlorophyll-*a* and phaeopigments in sediments are commonly found in the sediments of eutrophic estuaries under anthropogenic pressure, suggesting high primary production (Venturini *et al*., 2012; Silva *et al*., 2017). In the present study, chlorophyll-*a* was hardly detected in the sediments, on the other hand phaeophytin-a was elevated, especially at Jurujuba Sound. The inhibition of primary production by high turbidity levels is the probable cause of low levels of chorophyll-*a* in the bottom sediments of Jurujuba Sound, which, despite low depths presents very dark waters. Phytodetritus accumulation can also account for high concentrations of phaeopigments in the study area.

The evaluation of the trophic state of a marine environment only through the concentrations of nutrients in the water column may be masked by its dynamics. In comparison, sediments are natural nutrient sinks and can be very reliable to assess eutrophication aspects since they act as a geological register throughout time. Therefore, sediments play a key role in interpreting the environmental health of a coastal ecosystem, especially in relatively shallow environments. When it comes to phosphorus, the sorption of this nutrient by sediments is a crucial factor influencing its transport, degradation and fate in the aquatic system. The efficiency of coastal sediments in retaining phosphorus as well as the buffering effect between bottom sediments and water column concerning DIP is well documented and the preservation of P in the sediment compartment depends on a number of factors, such as DO at bottom waters, sedimentation rate, bioturbation, nature of P compounds supplied to the sediment/water interface and diagenetic processes (Boers *et al*., 1998; Froelich, 1988; Gardolinski *et al*., 2004). The sediments of urbanized coastal areas usually receive a mixture of labile and refractory organic and inorganic phosphorus, and some of these compounds are harder to degrade and thus behave as inert material and end up buried in their original form (Sundby *et al*., 1992). The internal contribution, in the form of released P adsorbed on bottom sediments can equally contribute or even exceed the contribution from external sources for the maintenance of eutrophication (Boers *et al*., 1988). Bottom sediments from Jurujuba Sound revealed a strong anthropic influence and the ability of retaining P, what is justified by the presence of fine sediments. The values of IP found in the present study are similar to the range of P concentrations registered at different sites at Guanabara Bay, such as the ones found by Carreira and Wagener (1998) around the Ipanema submarine outfall, 309-1498 $\mu g.g^{-1}$ and Borges *et al*. (2009) that found up to 1196 $\mu g.g^{-1}$ of total phosphorus with a contribution of ~90% of IP.

At Flamengo-Botafogo Sounds the predominance of OP suggests an elevated contribution of organic matter composed of refractory compounds such as humic substances, and probably not completely mineralized. Station F11, near Botafogo Beach, stood out with the highest concentrations of carbonate, TOC, IP, chlorophyll-*a* and phaeopigments, revealing a direct anthropogenic input at this location, probably due to Banana Podre and Berquó rivers that discharge directly into Botafogo Sound.

Eutrophication signs at bottom sediments of Jurujuba Sound were made explicit by elevated contents of TOC and inorganic phosphorus, both of them interacting with adjacent water to enhance this process and perpetuate this cycle as long as the anthropogenic supply of nutrients is maintained. At Flamengo-Botafogo Sounds bottom sediments cannot absorb most of the anthropogenic input due to the predominance of coarser particles, however the presence of elevated concentrations of organic phosphorus is also an indication of eutrophication.

5. CONCLUSIONS

The entrance of Guanabara Bay showed distinct characteristics regarding nutrient dynamics, mostly responding to two main factors: heavier nutrient loading through sewage input at Flamengo Botafogo Sounds, and differences between bottom sediments of the two areas influencing adsorption processes on nutrient dynamics.

Heavier anthropogenic input at Flamengo-Botafogo Sounds was evidenced by a higher concentration of dissolved inorganic phosphorus and dissolved inorganic nitrogen, mainly in the form of ammonium, probably derived from raw sewage. High concentrations of ammonium also seemed to play a key factor in phytoplankton biomass production at Flamengo-Botafogo Sounds, with primary production inhibited by elevated concentrations of this nutrient. Lower oxygenation of Flamengo-Botafogo waters compared to Jurujuba Sound also corroborated the hypothesis of heavier anthropogenic load at this location, with organic matter being mineralized along the deeper water column, decreasing dissolved oxygen levels.

Differences between grain size of bottom sediments from Jurujuba and Flamengo-Botafogo Sounds greatly influence nutrient dynamics at the entrance of Guanabara Bay. Fine sediments at Jurujuba Sound act as a trap for nutrient and organic matter absorbing excess anthropogenic discharge, helping to mask some eutrophication signs in the water column. At Flamengo-Botafogo Sounds coarser sediments retain less organic matter and inorganic nutrients; therefore, eutrophication signs are more evidenced in the water column. Overall, TRIX ranges were similar, revealing poor water quality at the entrance of Guanabara Bay, with a noticeable decrease from neap to spring tide. Results generated in the present study show the necessity of urgent public policies in order to mitigate eutrophication at Guanabara Bay.

AUTHORS CONTRIBUTION

Valquíria Aguiar: aquisição de dados primários, análises formais, escrita do artigo.

José Antônio Baptista Neto e Estefan Monteiro: Escrita do artigo.

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