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Evaluation of water quality and trophic state in the Parnaíba River Delta, northeast Brazil

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ABSTRACT

This study aims to assess the water quality and trophic state of the Parnaíba River Delta, in the Brazilian northeast, under different hydrological conditions. Surface water samples were collected from 16 sites along the river during 2011 and 2012 at the dry and rainy seasons. The obtained data showed a strong fluvial influence in practically the entire extension of the two deltaic channels. The water quality and trophic state classification was performed by adapting and calculating the Water Quality Index (WQI_{min}) and Trophic State Index ($TRIX_{PD}$). A Principal Component Analysis (PCA) and a Hierarchical Cluster Analysis (HCA) were conducted in order to adjust the index parameters. The WQI_{min} results presented medium to good ($70 \leq WQI_{min} < 90$) and bad to medium ($26 \leq WQI_{min} < 70$) water quality conditions for the different hydrological periods. The estuary is mainly limited by nitrogen ($N:P < 10$) in the dry season and by phosphorus ($N:P > 20$) in the rainy one. The results for $TRIX_{PD}$, showed a predominance of mesotrophic to eutrophic conditions in the estuarine system ($5 \leq TRIX_{PD} < 6$). This integrated approach can be a promising tool for assessing water quality and trophic status in tropical estuaries.

1. Introduction

Estuarine systems do not exist in isolation but as part of the continuum between the catchment area (the riverine system) and the coastal waters influenced by freshwater (Luu et al., 2012; Dabrowski et al., 2013; De Paula Filho et al., 2015a; Barroso et al., 2016). The complex hydrodynamics of these coastal environments transform them into temporary storage sites for suspended materials, nutrients and pollutants (Mitra et al., 2018; Gopal et al., 2018), while the main factor contributing to the high productivity rate of estuarine environments is the retention of nutrients (Eschrique, 2011; Luu et al., 2012; Marreto et al., 2017). Excess nutrients contribute to blooms of opportunistic microalgae that may release toxins, thus reducing natural biodiversity, damaging water quality and leading to a trophic imbalance (Figueiredo et al., 2006; Molisani et al., 2010; Luu et al., 2012; Barroso et al., 2016).

The Brazilian northeast is characterized by a semi-arid climate, with water availability becoming scarce during certain periods. This fact led to the construction of reservoirs for the storage of water for human use. Studies on aquatic ecosystems have, thus, focused mostly on the water quality of lentic water bodies in continental basins (Molisani et al., 2010; Rocha et al., 2015, 2016), while only few studies (Cotovicz Junior et al., 2012; Alves et al., 2013; Tavares et al., 2014) focused on the water quality of estuarine environments using numerical tools such as the water quality index (WQI) and the trophic index (TRIX).

Eutrophication is the process of enrichment of waters with nutrients, primarily nitrogen and phosphorus, which stimulates aquatic primary production (Vollenweider et al., 1998). The significant relevance of eutrophication processes in coastal marine waters has led to the development of several indices and models, such as the TRIX index (Vollenweider et al., 1998), the Assessment of Estuarine Trophic Status — ASSETS (Bricker et al., 2003), and the simplified index using pH and dissolved oxygen saturation (O'Boyle et al., 2013), have been used to establish the trophic status in coastal regions.

The TRIX index was applied in coastal waters of several temperate countries, as on the Almargem coastal lagoon in Algarve, Portugal (Coelho et al., 2007), on the coast of Sicily (Caruso et al., 2010) and on the Thames estuary (Devlin et al., 2011), as

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well as in tropical estuaries in Yucatán, Mexico (Herrera-Silveira and Morales-Ojeda, 2009). Furthermore, the TRIX index has been systematically applied to determine the trophic status of estuaries along the Brazilian coast (Cotovicz Junior et al., 2012; Alves et al., 2013; Tavares et al., 2014).

The complexity involved in water quality analysis and assessment, as well as the enormous amount of data and information that needs interpretation, has made the use of indices increasingly popular when it comes to identifying water quality trends and changes (O'Boyle et al., 2013; Cotovicz Junior et al., 2012; Rocha et al., 2015, 2016; Marreto et al., 2017). Environmental agencies (ANA, 2012; CETESB, 2018) and researchers have used water quality indices (WQI's) and the Trophic State Index (TRIX) as tools for the management of water resources (Caruso et al., 2010; Cunha et al., 2013; O'Boyle et al., 2013; Rocha et al., 2015, 2016; Marreto et al., 2017).

Water quality and trophic state indices integrate information provided by a combination of several sub-indices (quality variables) into a univariate expression. These sub-indices should include the most significant parameters of the dataset so that the index can describe the overall status, reflecting changes in a representative manner (Pesce and Wunderlin, 2000; Caruso et al., 2010; O'Boyle et al., 2013; Cunha et al., 2013; Rocha et al., 2015, 2016). These indices are the main tools used in the decision-making process involving water resources, contributing to the establishment of environmental policies and helping in the management of water resources at local (Simões et al., 2008; Rocha et al., 2016), regional (Medeiros et al., 2017; CETESB, 2018) and national levels (ANA, 2012; Dabrowski et al., 2013). All these tools (models) require data to derive both their exogenous variables and estimates of their endogenous variables (parameters) (Vollenweider et al., 1998; O'Boyle et al., 2013; Cunha et al., 2013; Rocha et al., 2016).

Establishing baseline conditions in rivers and their estuaries is fundamental for conciliating water uses with human health, environmental services, and the biodiversity maintenance and management aspects in the watersheds (Cunha et al., 2012; Dabrowski et al., 2013). Water quality monitoring is a fundamental and primary stage for establishing the baseline status of an aquatic body revealing how anthropic activities modify the environmental integrity, carrying capacity and environmental services of an aquatic ecosystem (Rocha et al., 2016; Medeiros et al., 2017; Mitra et al., 2018).

The Resolution 357/2005 of the Brazilian National Environment Council (BRASIL, 2005) provides a set of water quality parameters that allow comparisons between actual environmental conditions and the ideal ones, showing the responses of the aquatic environments to the anthropic impacts on them (Cunha and Calijuri, 2010; Cunha et al., 2013). Many studies have evaluated the percentage risk of disagreement, or non-compliance, between the monitoring results and the regulatory quality standards (Borsuk et al., 2002; Zhang and Arhonditsis, 2008; Cunha and Calijuri, 2010; Cunha et al., 2012). In this sense, quality or probability curves can be useful in the management of coastal water resources (Cunha and Calijuri, 2010; Cunha et al., 2012).

The overall aim of this study is to apply the tools based on the water quality (WQI_{min}) and trophic state (TRIX) indices to assess the quality and ecological status of the coastal waters of the Parnaíba River Delta. This tropical estuary is a national environmental protection area of significant ecological and economic importance of the semi-arid coast of northeastern Brazil

2. Materials and methods

2.1. Study area

Our study was conducted on the Parnaiba River delta, a tropical estuary located in the Brazilian semi-arid coast between the states of Ceará, Piaui and Maranhão (Fig. 1). The local climate alternates between a dry season (spring and summer), and a rainy season (fall and winter). The Parnaíba River runs over 1450 km and has a drainage basin of 331,441 km^2, ending in a delta-type mouth, which has two main river channels running into the Atlantic Ocean, i.e. the Igaraçu (Ig) and the Parnaíba (P). The delta extends over 2700 km^2 and is formed of more than 70 islands, being the only delta in the Americas exposed to the open sea and one of the three largest in the world (Farias et al., 2015). The delta area supports large areas of mangrove swamps, characterized by its role in sediment retention, filtration of organic matter, nutrients and trace metals (De Paula Filho et al., 2015a,b). The estuary has a meso-tidal regime and has average depth of around 4.0 m. Due to its characteristics (winds, bathymetry and shear flow), the estuary is classified as partially mixed (Knoppers et al., 2009).

A regional urban center with approximately 150,000 inhabitants (Parnaíba City) is located on the western boundary of the environmental protection area. There are few point sources of contaminants and diffuse pollution sources prevail, which are typically difficult to control and monitor (De Paula Filho et al., 2015a,b). The major environmental impacts are the release of domestic effluents, deforestation and erosion. In this regard, the negative effects of the release of domestic and industrial effluents into the water system should not be neglected (De Paula Filho et al., 2015a,b).

2.2. Sample collection and processing

Two sampling campaigns were carried out in September 2011 and in March 2012, at the dry and rainy seasons, during spring tides. Eight surface water samples were collected at each of the estuarine channels, i.e. the Parnaíba (sampling stations P1–P8) and Igaraçú rivers (sampling stations Ig1–Ig8). The average water discharge during the sampling campaigns was 324 $m^3\ s^{-1}$ and 1179 $m^3\ s^{-1}$ for the dry and rainy seasons, respectively (SNIRH, 2018).

The physical and chemical variables were determined in situ using portable probes. Water temperature (T), dissolved oxygen (DO) and oxygen percent saturation (D%O) were measured with a Hanna HI 9143 probe. Turbidity (NTU) was measured with a Hanna 93703 turbidimeter, the salinity (S) with a Hanna HI 9835 multisound, and the pH with a portable Hanna HI 8424 meter with automatic temperature compensation. Total suspended solids (TSS) were determined on discrete water samples collected in triplicate using 1.0 L PET bottles. Samples were all filtered with pre-weighed Whatman GF/F fiber filters (0.7 μm pore size) — the filters were dried at 45 °C and weighed for determination TSS (mg L^{-1}) (Strickland and Parsons, 1972). The water samples were collected from the sub-surface, at a depth of approximately 30 cm, using a Van Dorn bottle. Samples were then stored in amber glass bottles and cooled in an ice bath at about 4 °C in isothermal boxes during field transport (ANA, 2011) for determination of total phosphorus (TP) and total nitrogen (TN), according to the method proposed by Valderrama (1981).

2.3. Data analysis and indices

2.3.1. Water quality curves

Water quality curves were generated using the data collected in the sampling campaigns. The critical variables with the highest occurrence of nonconformity between the tested concentrations and the respective upper or lower limits established by Brazilian regulations were identified (BRASIL, 2005; Silva and Jardim, 2006; Cunha and Calijuri, 2010; Simões et al., 2008).

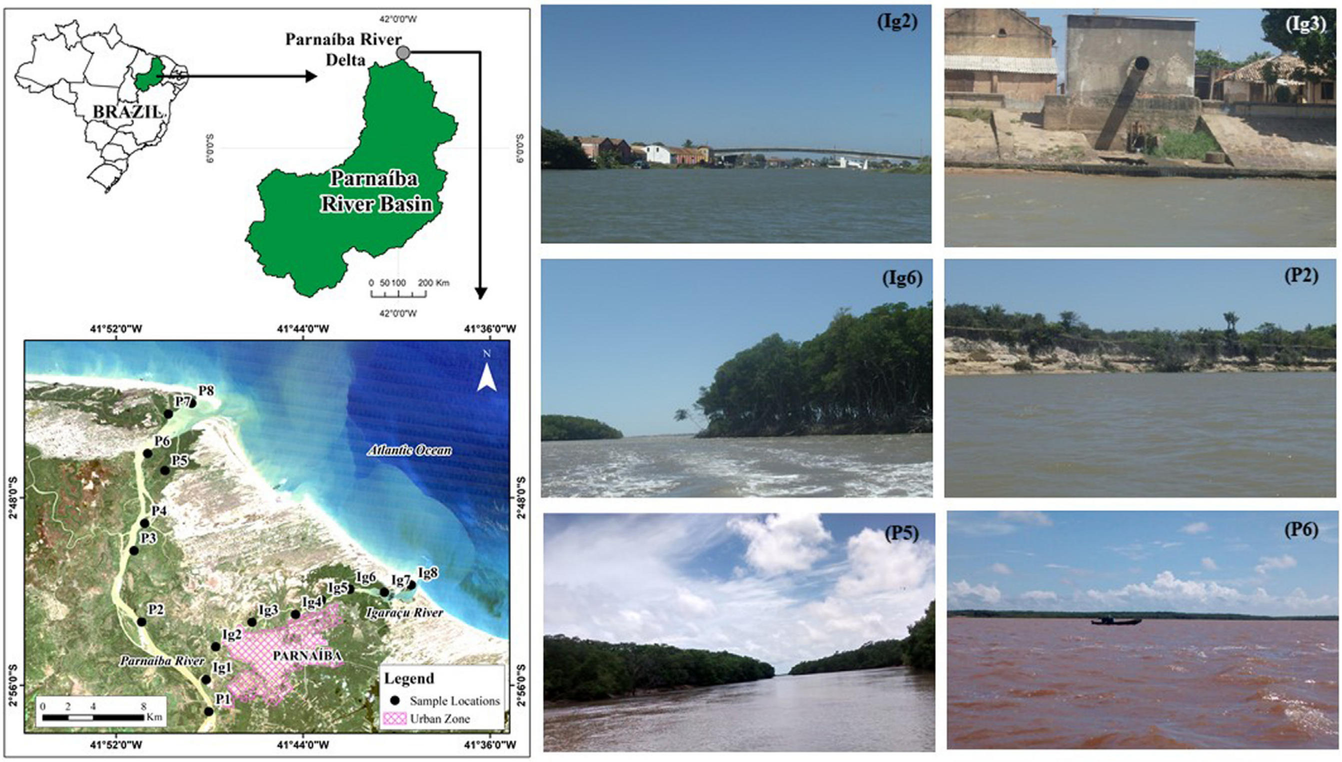

Fig. 1. Location map and sampling sites distributed along the two main channels of the Parnaíba River Delta estuary, on the Atlantic coast of Northeast Brazil.

In order to calculate the probability curves, we used the cumulative distribution function $\mathbb{F}(\mathcal{X})$, capable of describing the probability distribution of a random variable with an actual value $\mathcal{X}$, according to Eq. (1) below:

$$\mathbb{F}(\mathcal{X}) = \mathcal{P}(\mathcal{X} \le \boldsymbol{x}) \tag{1}$$

where $\mathcal{P}(\mathcal{X} \le \boldsymbol{x})$ represents the probability that the variable $\mathcal{X}$ will have a value lower than or equal to an established $\boldsymbol{x}$. The probability results demonstrate the exceedance or non-exceedance of the value of F(X) to the value of x, relative to the quality criteria, in this case according to Brazilian regulations, for a Class 1 stream. Values and respective curves were calculated for each variable.

2.3.2. Minimum Water Quality Index ($WQI_{\boldsymbol{min}}$)

The minimum Water Quality Index (WQI_{min}) (Pesce and Wunderlin, 2000) was used to determine the surface water quality conditions. The WQI_{min} was determined from the information obtained in the water quality curves. The index was calculated as per Eq. (2), adding normalized values of three or more variables (Pesce and Wunderlin, 2000; Simões et al., 2008).

$$\mathbf{WQI}_{\boldsymbol{min}} = \frac{(\boldsymbol{C}_{v1} + \boldsymbol{C}_{v2} + \boldsymbol{C}_{v3} + \cdots . + \boldsymbol{C}_{vn})}{\boldsymbol{n}} \tag{2}$$

where $\boldsymbol{C}_v$ is the normalized value relative to a given water quality critical variable in the deltaic system and $\boldsymbol{n}$ is the number of variables involved in the calculation. The normalizing factors for the WQI_{min} calculation were obtained from Table 1.

The quality classification was based on the ranges of values and their respective conditions, where $WQI_{min} \le 25$ is very bad, $26 \le WQI_{min} \le 50$ is bad, $51 \le WQI_{min} \le 70$ is regular, $71 \le WQI_{min} \le 90$ is good, and $91 \le WQI_{min} \le 100$ is rated as excellent (ANA, 2012; CETESB, 2018).

2.3.3. Nutrient stoichiometry (N:P)

The relative molar concentrations of N and P have been used to estimate which of these nutrients is limiting the growth of algae in aquatic systems (Redfield, 1958). Nutrient dynamics in estuaries are different from those of oceanic systems, in light of the diversity and composition of the estuarine biota (Burford and Rothlisberg, 1999). A N:P ratio of 10 to 20 is a balanced one, while ratios below 10 indicate nitrogen as a limiting nutrient and ratios exceeding 20 indicate phosphorus as limiting (Sundareshwar et al., 2003). The stoichiometric N:P molar ratio was determined to identify which nutrient has the greatest impact on primary production.

2.3.4. Trophic index — TRIX

The trophic index (TRIX) (Eq. (3)) calculations were done after: (i) compilation of the data obtained in computational worksheets; (ii) determination of dissolved oxygen values as absolute deviation [%] of saturation ($aD\%O$) [$Abs\,|100 - \%O| = aD\%O$]; (iii) conversion of the Total Nitrogen (mg m^{-3}) and Total Phosphorus (mg m^{-3}) concentrations; (iv) elimination of outlier values that are not within the range determined by the average value ± 2.5 times the standard deviation of each analyzed variable; (v) determination of the log_{10} of the values of the tested variables after the elimination of the outliers and calculation of the minimum, mean, maximum and standard deviation of the logarithmic values; (vi) determination of the factors k and m (Vollenweider et al., 1998).

$$TRIX = \frac{\log_{10}(Chla \times aD\%O \times TN \times TP) - k}{m} \tag{3}$$

The classification scale adopted consider five trophic state categories, ranging from Excellent: < 2 (ultra-oligotrophic); High: $2 < TRIX < 4$ (oligotrophic); Good: $4 \le TRIX < 5$ (Mesotrophic); Moderate: $5 \le TRIX < 6$ (Mesotrophic to Eutrophic); and Poor: $6 \le TRIX < 8$ (Eutrophic) (Caruso et al., 2010).

Table 1
Normalizing factors for the variables monitored and used in the WQI_{min} calculation.

Parameter	Normalization factor (C_i)										
	100	90	80	70	60	50	40	30	20	10	0
	Analytical value[a]										
DO	≥7.5	>7.0	>6.5	>6.0	>5.0	>4.0	>3.5	>3.0	>2.0	≥1.0	<1.0
TN	<0.4	<0.7	<1	<1.5	<5	<10	<15	<20	<30	≤35	>35
pH	7	7–8	7–8.5	7–9	6.5–7	6–9.5	5–10	4–11	3–12	2–13	1–14
TP	<0.16	<1.60	<3.20	<6.40	<9.60	<16.0	<32.0	<64.0	<96.0	≤160.0	>160.0
TSS	<250	<750	<1000	<1500	<2000	<3000	<5000	<8000	<12.000	≤20.000	>20.000
NTU	<5	<10	<15	<20	<25	<30	<40	<60	<80	≤100	>100
T	21/16	22/15	24/14	26/12	28/10	30/5	32/0	36/−2	40/−4	45/−6	>45/<−6

[a] TP, TN, DO and TSS (mg L^{-1}); Temperature (°C); Turbidity (Nephelometric Turbidity Unit — NTU). (Pesce and Wunderlin, 2000; Silva and Jardim, 2006; Simões et al., 2008).

2.4. Statistical data processing

The Microsoft Excel® software was used for the pre-treatment of data. Data normality was tested using the Shapiro–Wilk test. The Student *t* and the Mann–Whitney–Wilcoxon tests were applied to identify any statistical differentiation between the means of the hydrochemical variables ($p < 0.01$). The significance of the association between pairs of variables was assessed using the Pearson correlation test ($p < 0.05$). Spatial trends were analyzed by simple linear regression. The Principal Component Analysis (PCA) and the Hierarchical Cluster Analysis (HCA) were performed to adjust the index parameters. All statistical analyzes was done with the Statistica 8.0 software (StatSoft, Inc. 1984–2007). The maps were prepared with the ArcMap SIG ArcGis 9.0 package. The distribution of colors by values was done by applying the graduated colors method. All maps are drawn using the geographic coordinates system with horizontal WGS 84 datum.

3. Results

3.1. Hydrochemical behavior of the monitored variables

The data obtained from the analytical studies were subjected to descriptive statistics such as seasonal mean and standard deviation (σ). The water quality parameters and the regulatory limits for the hydrochemical variables, as well as the descriptive statistics of the sixteen sampling stations, are summarized in the supplementary material (Tables S1, S2 and S3). The Shapiro–Wilk test was applied to all parameters, with Salinity being the only non-normal one. The Student *t* test and the Mann–Whitney–Wilcoxon test ($p < 0.01$) show that TSS, TN and S did not present statistical differences among the means in the different sampling campaigns. On the other hand, pH, T, NTU, DO, D%O and TP showed statistically significant differences.

High temperatures prevailed in both sampling campaigns, ranging between 26.5 °C and 29 °C (mean 28 ± 0.7 °C). Pearson's rank test (see Supplementary Material — Table S4) revealed a significant correlation between Temperature and Turbidity ($r = 0.61$, $p < 0.01$), DO ($r = -0.43$, $p < 0.05$), D%O ($r = -0.42$, $p < 0.05$) and TP ($r = -0.65$, $p < 0.01$). The warm temperatures of the waters of the Parnaíba River Delta can be attributed to a series of factors, such as solar radiation intensity, which in the Brazilian northeast is 18 MJ m^{-2} on average, atmospheric temperature, sunlight exposure time, evaporation rate and inflows from adjacent tributaries (Pereira et al., 2006).

The pH values were within the regulatory range, ranging from 7.2 (P4, dry season) to 8.5 (P2, rainy season) with an average of 7.7 ± 0.3. Significant positive correlations were found between pH and Turbidity ($r = 0.35$, $p < 0.05$), TSS ($r = 0.39$, $p < 0.05$), D%O ($r = -0.35$, $p < 0.05$) and TP ($r = -0.37$, $p < 0.05$). The pH values during the rainy season were in general higher than those found in the dry season. pH values above 8.0 were recorded only in the second sampling campaign at points P1, P2, P4, P7, P8 and Ig1. The highest pH values were recorded at P1 and Ig1, located on the upper estuary, reflecting the influence of the basin's drainage water that transports dissolved ions and suspended materials to the Delta.

The Turbidity measurements ranged from 5 NTU (P3, dry season) to 61 NTU (P6, rainy season) with an average of 23 ± 18 NTU. Statistically significant correlations were found with DO ($r = -0.67$, $p < 0.01$), D%O ($r = -0.71$, $p < 0.01$) and TP ($r = -0.65 p < 0.01$). The results obtained in the first sampling campaign were up to an order of magnitude lower than those obtained during the rainy season. In both campaigns the turbidity presented an increasing trend following the estuarine gradient. TSS varied between 28.6 mg L^{-1} (P8, rainy season) and 111 mg L^{-1} (P4, rainy season) with an average of 60 ± 24 mg L^{-1}. There was a significant correlation with D%O ($p < 0.05$). In terms of spatial distribution, the results point to a decreasing trend of the TSS values from the upper to the lower estuary in both seasons, except for the Igaraçu river in the dry season.

The dissolved oxygen of the Parnaíba River Delta ranged from 2.9 to 10.0 mg L^{-1}, with a mean of 6.1 ± 0.7 mg L^{-1}. In the dry season campaign, there was a significant increasing trend of DO concentrations in both channels following the estuarine gradient. The DO concentrations measured in the rainy season were up to 2.6 times lower than those found in the dry season. A similar behavior was recorded for oxygen saturation. The D%O varied between 31% and 115%, with an average of 75 ± 23%. A strong positive correlation was found between DO ($r = 0.98$, $p < 0.01$) and D%O ($r = 0.71$, $p < 0.01$), in relation to TP.

The TP concentrations from both campaigns ranged from 0.01 mg L^{-1} to 0.35 mg L^{-1}, with a mean of 0.11 ± 0.09 mg L^{-1}. The results obtained in the dry season were up to 9.2 times higher than those recorded in the rainy season. Nutrient concentrations were generally higher in the Igaraçu River in both sampling campaigns. TN concentrations were reasonably stable seasonally. TN concentrations ranged from 0.3 mg L^{-1} to 0.78 mg L^{-1}, with a mean of 0.47 ± 0.11 mg L^{-1}. Both nutrients showed a trend of increasing concentrations from the upper to the lower sections of the estuary in both seasons, except for TN in the Igaraçu river in the dry season.

3.2. Predicting the frequency of water quality regulatory violations

A probabilistic analysis of the conformity or nonconformity (for Class 1 streams) was carried out, aiming to identify the system's water quality critical variables (Fig. 2a, b, c). The curves were plotted based on the accumulated distribution function using all the available data (Borsuk et al., 2002; Silva and Jardim, 2006; Cunha and Calijuri, 2010). The pH and TN values were within the regulatory range (6.0–9.0) and upper limit (2.18 mg N L^{-1}), respectively (See Supplementary Material — Table S1), and therefore these variables are not critical to the quality of the

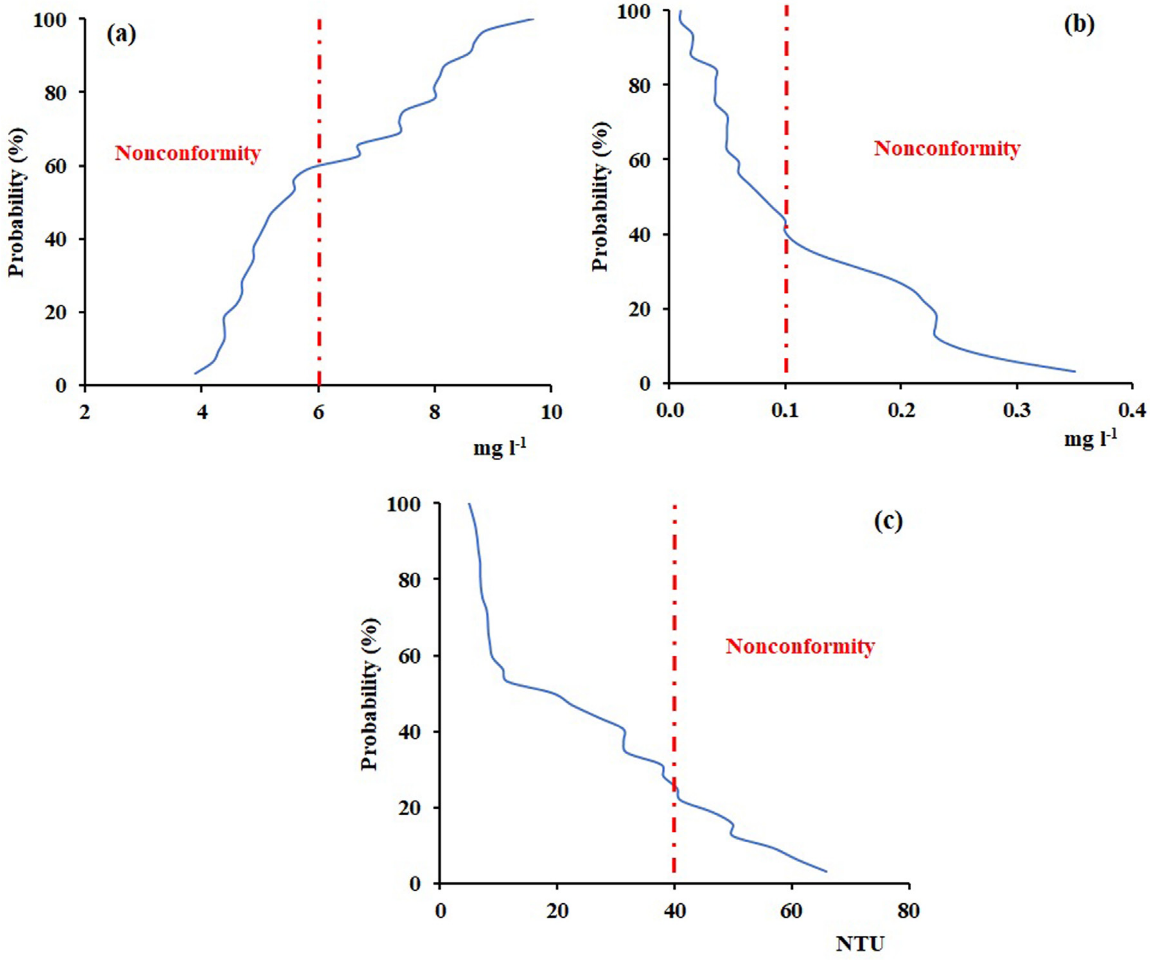

Fig. 2. Water quality (conformity or nonconformity) or probability curves for the Parnaíba River Delta estuary. (a) Dissolved Oxygen, (b) Total Phosphorus, and (c) Turbidity. The red lines show the regulatory limits for a Class 1 stream.

aquatic system. On the other hand, DO (Fig. 2a), TP (Fig. 2b) and NTU (Fig. 2c) are considered critical water quality variables.

TSS was within the regulatory limit established for Class 1 streams, i.e. below 500 mg L^{-1}, while turbidity was variable with 25% of the measurements exceeding the upper limit for Class 1 streams (40 NTU). Dissolved Oxygen results show that 60% of the measurements had a probability of being below 6.0 mg L^{-1}, i.e. not within the regulatory requirement.

There was an increase in the phosphorus concentrations along the longitudinal axis of estuary flow, indicating a nutrient enrichment. Around 40% of the TP results were above the regulatory upper limit for Class 1 streams (0.1 mg L^{-1}) and were restricted to the dry season with high values at sites Ig2–Ig8 at the Igaracu River and at sites P5–P8 of the Parnaíba deltaic channel. Only two sites (Ig1 and P4) were lower than the regulatory limit.

The scree plot of the PCA characteristic's roots (eigenvalues) was used to identify the number of PCs to confirm or eliminate the critical water quality variables (Table 2). Three components were extracted based on the scree plots and eigenvalues. The most important, i.e. Factors I and II, or main components associated to the data matrix, explained 62% of the total variance relative to the original variables. These factors show that the main variables influencing the water quality of the estuary are NTU, TP and DO (or D%O), which are the critical variables we used to calculate the WQI_{min} for the system.

The dendrogram, based on the cluster analysis results, strengthens the strong association between the ecological parameters (Fig. 3) and supporting PCA findings. Cluster I reinforces the strong association between DO, D%O and TP, expressed by the correlation values, corroborating the matrix of the main components by including TN as a significant factor within the $TRIX_{PD}$ index (Table 2). Cluster II shows the relationship between Temperature and Turbidity, and the influence of TSS on the pH conditions of the system.

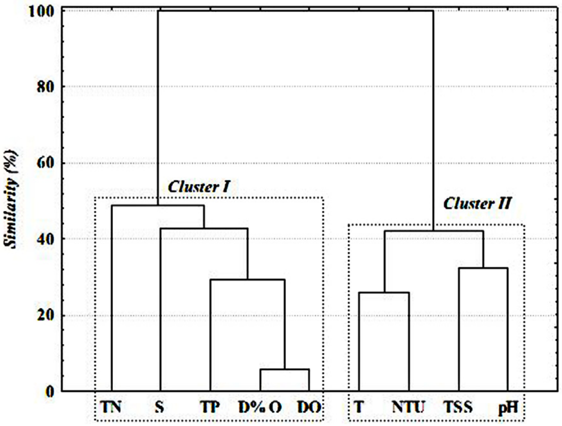

Fig. 3. Dendrogram showing the cluster between the water quality ecological parameters of the Parnaíba River Delta and its similarities.

Table 2
PCA of environmental variables on the three varimax-rotated PCs for water quality data from the Parnaíba delta estuary.

Parameter	Factor I	Factor II	Factor III
pH	−0.468	−0.568	0.117
NTU	**0.833**	0.77	−0.208
TSS	−0.492	−0.223	0.637
T	−0.662	0.211	−0.437
DO	**0.902**	−0.041	−0.041
D%O	**0.901**	0.021	−0.068
TP	**0.840**	−0.010	0.242
TN	0.179	**0.782**	0.027
S	0.380	−0.602	−0.530
Eigenvalue	4.131	1.408	1.001
Variance	0.459	0.156	0.111

Extraction method: Principal Component Analysis.
Rotation method: Varimax with Kaiser normalization.
Bold letters: The most significant factor loadings.

3.3. Water Quality Index (WQI_{min})

There was a predominance of good conditions (56%) in the first campaign (dry season) (Fig. 4), based on WQI_{min}. In the Parnaíba River (P) WQI_{min} ranged from 63 (P2) to 80 (P4 and P8), with a quality improvement trend along the estuarine gradient. An inverse trend was observed in the Igaraçu river, with results ranging from 57 (Ig7) to 87 (Ig1) in the same period.

The WQI_{min} indicates bad to medium water quality conditions for most samples during the rainy season. In the Parnaíba River the values varied between 47 (P6) and 67 (P7) while in the Igaraçu River they ranged from 50 (Ig4 and Ig5) to 60 (Ig8). In the rainy season, the number of medium quality records practically doubled, reaching 82% of the total.

3.4. Trophic state indices

In the Parnaíba channel, the N:P molar ratios (Fig. 5a) in the rainy season were higher (mean = 45) than those found in the dry season (mean = 8.0). In both cases we saw an increasing trend from the upper to the mid estuary (P1 → P5). In the Igaraçu river, the N:P ratios presented a decreasing trend from the upper to the lower section of the estuary (Fig. 5b), while the average N:P ratio found in the rainy season was 22, exceeding that of the dry season (8.0).

These results demonstrate the Parnaiba River Delta is a highly dynamic environment regarding nutrient availability, with seasonal changes to the limiting nutrient. Nitrogen was the limiting factor in the dry season (N:P $<$ 10:1), mainly in the lower-mid portion of the estuary, except in P3, P4 and Ig2, in which the river shows a balanced ratio (10 $<$ N:P $<$ 20). The opposite occurs during the rainy season, which has higher flow rates and where phosphorus is the limiting nutrient (N:P $>$ 20), except for P1, P6 and Ig6, where there was a balance of nutrient availability for primary production.

The trophic index adapted to the tropical estuary of the Parnaíba River Delta ($TRIX_{PD}$) is given by Eq. (4), which considered the dataset of TN, TP and D%O from the two sampling campaigns. The values of the calculated coefficients k and m were equal to 3.7 and 0.41, respectively (See Supplementary Material — Table S5).

$$TRIX_{PD} = \frac{\log\left(aD\%O \times TN \times TP\right) - 3.7}{0.41} \tag{4}$$

The mean values of the $TRIX_{PD}$ index were 5.5 and 5.3 for the dry and rainy seasons, respectively. Mesotrophic to eutrophic conditions prevailed in both seasons. The spatial analysis by sampling point reveals a variability of the trophic conditions at the different sectors of the estuary (Fig. 6). The $TRIX_{PD}$ spatial distribution followed the seasonal water quality reduction trend.

In relative terms, the results obtained in September 2011 showed that 13% of the sampling points were oligotrophic, 31% mesotrophic, 25% meso-eutrophic and 31% eutrophic. In March 2012, oligotrophic conditions were recorded in only 6% of the sampling sites, while 25% of the sites were mesotrophic, 38% meso-eutrophic and 31% eutrophic.

4. Discussion

The behavior of the different variables in the two sampling campaigns was evaluated to determine the quality and trophic state indices of the Parnaíba River Delta estuary. Despite the marked contrast in the seasonal waterflow, the data exhibited a strong fluvial influence in practically the entire extension of the two channels (Parnaíba and Igaraçu). Values of zero salinity were found near the Delta's mouth (P7, P8 and Ig7) in both seasons, and from there the salinity level rose from the seawater and tidal influx area of influence.

Nonetheless, there was a marked change in the temperature gradient between the two sampling seasons. In the dry season we found a temperature decreasing trend along the estuarine gradient, being lower near the mouth of the estuary. This is related to the effect of the weaker flow, allowing the colder seawater to lower the temperature at the mouth of the estuary (Gopal et al., 2018). The opposite was observed in the season with a higher rainfall intensity.

No marked pH seasonal variability was observed, with slightly alkaline characteristics prevailing. The data reflects the marine influence in raising the pH of the estuarine waters, mainly from the mid estuary (P4, Ig4). This was not observed during the rainy season, when we saw a reduction in pH following the river-to-sea flow. The pH range was neutral to sub-alkaline (7.2–8.5) and within the range (6.5–8.5) prescribed by World Health Organization guidelines (WHO, 2008). Similar alkaline pH values were reported by other authors for estuarine environments in the Brazilian northeastern coast. Marins et al. (2003) found pH values above 8.0 in the Jaguaribe River estuary. Figueiredo et al. (2006) obtained pH values ranging from 8.0 to 8.8 in the Itamaracá estuarine complex, and Noriega et al. (2005) observed pH values ranging from 7.4 to 7.8 in the waters of the Jaboatão River estuary.

The results demonstrated a reasonable stability of TN surface water concentrations. This fact may be related to the significant downstream contribution of nitrogen loads, mainly due to the inefficient sewage treatment system in the region. Barroso et al. (2016) evaluated the effects of river flow on the availability of nutrients in estuaries in northeastern Brazil, finding higher TN concentrations in coastal areas with strong urban influences. In areas subjected to intense agricultural soil use, the highest TN concentrations were found during the rainy season (Lacerda et al., 2008). TN showed non-significant correlations with most of the hydrochemical variables investigated.

The study of individual hydrochemical variables presents difficulties when it comes to establishing the quality of a given water body, hindering the water management and decision-making process (Silva and Jardim, 2006). The application of quality indices to classify the ecological and trophic statuses reduces the level of uncertainty generated by the observation of individual variables. In this study, the adaptation of a quality index for the Parnaíba River Delta's waters is simplified by considering only the critical environmental variables affecting this water body at a given moment. The PCA analysis and the probability curves for the monitored variables showed the water quality characterization can be made from a reduced number of variables critical to the system (Fig. 2, Table 2). Furthermore, working with an index that

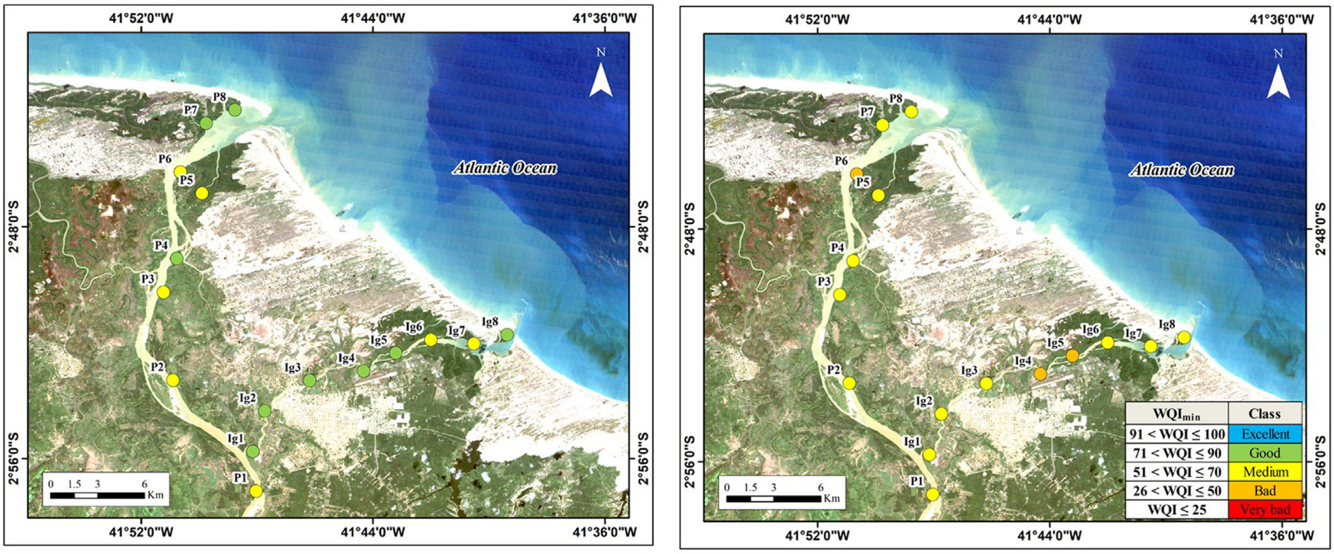

Fig. 4. Spatial variation of the WQI$_{min}$ index for the sampling stations on the Parnaiba River Delta. Dry (left) and rainy (right) seasons.

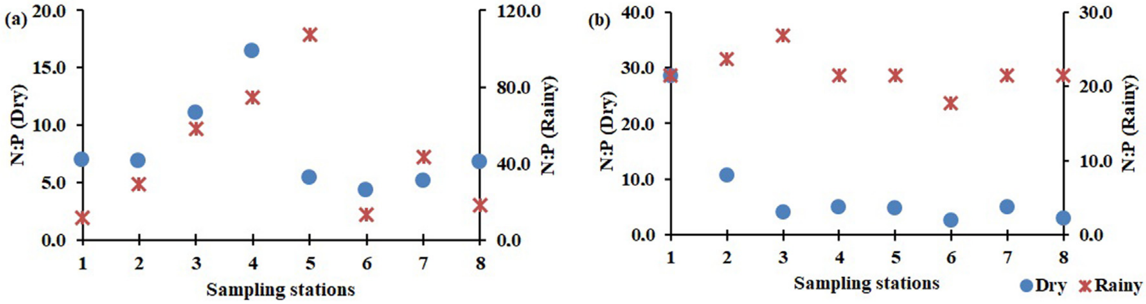

Fig. 5. Spatial behavior of N:P ratios in surface waters of the Parnaíba River Delta in different hydrological periods. (●) Dry season; (✖) Rainy season. (a) Parnaíba River and (b) Igaraçu River.

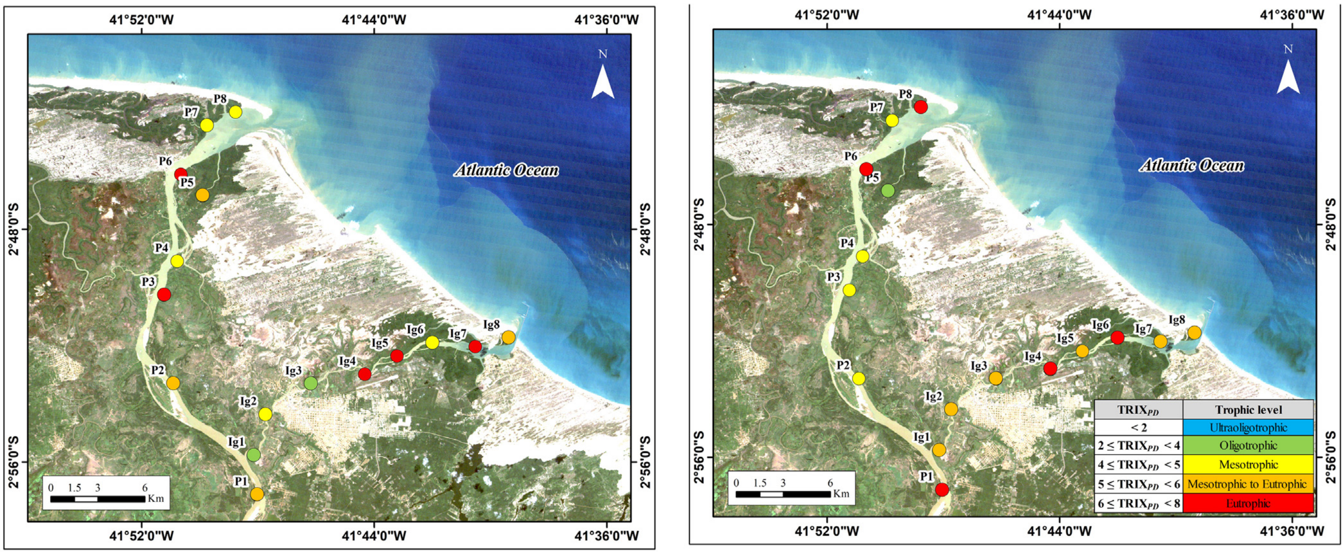

Fig. 6. TRIX$_{PD}$ Spatial variation along the sampling stations in the two estuarine channels. Dry (left) and rainy (right) seasons.

uses fewer environmental variables reduces the classic undesirable eclipse effect (Pesce and Wunderlin, 2000). The eclipse effect results from the process of aggregating too many environmental variables into a single factor leading to an attenuation of the negative impact of one variable as it is offset by the stable behavior of the others. Our results are consistent with this premise, as the behavior analysis and the probability curves of the monitored variables showed that the water quality characterization of the Parnaíba River Delta system can be attained by using just DO, TP and NTU.

In both sampling campaigns, the DO and D%O readings showed an increasing trend from the upper to the lower estuary. However, in the dry season this behavior was more pronounced due to the weaker river flow. Such weaker river flow increases the marine penetration with the agitation and intermixing of saline and fresh water, elevating the DO concentrations downstream (Marins et al., 2003). When formulating the WQI for the different monitoring sites, DO was the variable contributing the largest weighting factor (Table 1) in the dry season, while the opposite situation was found to occur in the rainy season.

Total phosphorus concentrations were higher in the dry season, increasing along the estuarine gradient and with maximum peaks at P7 and Ig6, resulting in low weighting factors used in the calculation of WQI in both estuarine channels. In the rainy season, with stronger river flows, TP showed higher concentrations at the innermost sampling sites of the estuary (P1 and Ig2). The lower mean value for TP in the rainy season is a result of the adsorption of phosphates onto reactive sites of clay minerals present in the suspended matter, thus contributing to its partial sequestration from the aquatic compartment (Marins et al., 2007; Gopal et al., 2018). The mean TP concentrations were higher in the Igaraçu River, probably because of the direct urban influence of the city on its right bank. Parnaíba City has the largest urban density in the region and has inadequate sewage treatment facilities, which serve less than 10% of the city's population (SNSA, 2016).

The mean turbidity during the rainy season (41 NTU) was five times higher than that of the dry season (8 NTU). The excess of solids in the water affects the aquatic biota, as it may affect the luminosity conditions in the water column, thus interfering with the metabolism of underwater autotrophic organisms by hindering photosynthesis (Burford and Rothlisberg, 1999; Barroso et al., 2016). This in turn may negatively affect all other heterotrophic organisms dependent on the dissolved oxygen produced by photosynthesis. This fact results in a negative correlation between these variables (see Supplementary Material — Table S4).

The non-conservative behavior of phosphorus in the estuarine environment is shown by its negative correlation with NTU. Key processes responsible for this non-conservative behavior include burial in sediment reservoirs and desorption processes, particularly in nutrient-rich sediments. Generally, freshwater nutrients are found mainly in particulate form (i.e. linked to suspended mud particles) and may be released when exposed to a saline water solution (Wolanski et al., 2006).

The spatial distribution of WQI_{min} (Fig. 3) in the dry season showed higher quality classes in the estuarine channels, especially in the Igaraçu river. The higher dissolved oxygen levels in its waters, in comparison to the Parnaíba river, have improved the WQI_{min}. On the other hand, it was evident that the greater contribution of freshwater to the estuary due to the more intense rains in the second campaign resulted in a lesser water quality throughout the estuary. The additional organic and mineral inputs from the drainage of the upstream basin reach the estuary and affect the hydrochemistry of the system (Marins et al., 2007; Lacerda et al., 2008). The sampling sites with a poor water quality may reflect the disposal of domestic sewage and urban drainage upstream and from Parnaíba City. A drastic reduction in the WQI_{min} of the Igaraçu estuarine channel in the rainy season was observed, with the Ig4 and Ig5 sampling points showing a particularly poor water quality. These points are downstream to Parnaíba City, reflecting the fact that this river is used to dispose domestic sewage and urban drainage from this urban center (Fig. 1). The discharge of raw sewage into coastal waters is one of the factors most frequently contributing to the degradation of their water quality, which may lead to increased eutrophication processes triggered by the increased availability of nutrients (Gopal et al., 2018; Mitra et al., 2018).

Nitrogen and phosphorus limitation was seasonally dependent (Fig. 4). Redfield's N:P ratio presented an average value of 8:1 in the dry season and 33:1 in the rainy season. Nitrogen limitation was observed in the dry season acting as a regulating factor for microphytoplanktonic production in estuarine systems, affecting the trophic state of such systems (Burford and Rothlisberg, 1999; Figueiredo et al., 2006). As previously indicated, phosphorus became the limiting nutrient in the rainy season. One of the probable factors may be related to its geochemical reactivity, leading to the reduction of its bioavailability. In the dry season the highest TN concentrations at points P3 and P4 (see Supplementary Material — Table S2) contributed to raise the N:P ratio in the Parnaíba channel, resulting in a balanced condition (Fig. 4a). In addition, other associated processes that could be affecting the distribution of nitrogen and phosphate compounds could be the vertical mixture produced by wind, the sedimentation of phosphate compounds in association with other compounds, and the remineralization of organic matter (Nascimento et al., 2003; Noriega et al., 2005).

Surveys conducted in the Brazilian northeast coast, in areas submitted to different levels of anthropic intervention, reported results similar to those observed in the Parnaíba River Delta. A study by Melo-Magalhães et al. (2016) conducted in the São Francisco estuary, which is also subjected to the semi-arid conditions of northeastern Brazil, showed a limitation by phosphorus in the rainy season and by nitrogen in the dry season. Eschrique (2011), studying the estuary of the Jaguaribe River, observed N:P ratios $>$20:1 in the dry season and $<$10 in the rainy season, corroborating the pattern observed in our results.

Considering the $TRIX_{PD}$ results, the waters of the Parnaíba estuary can be classified as moderately to highly productive. The mean values of the index were within 5 and 6. As a matter of fact, mesotrophic to eutrophic conditions prevailed in the system (Fig. 6), mainly in the Igaraçu channel during the rainy season. When considering the trophic behavior of the estuarine channels during the dry season, the $TRIX_{PD}$ values for the Parnaiba river ranged between 4.3 (P4) and 6.4 (P6), while the most productive sites were on the upper estuary (Fig. 6a). In the Igaraçu river, the index ranged from 3.2 (Ig1) to 9.1 (Ig5), with an increasing trend of the trophic state following the fluvial-marine gradient. The sampling sites located downstream to the city of Parnaiba showed more elevated trophic levels (sampling points Ig5 and Ig7, with a $TRIX_{PD} = 7.5$).

Both deltaic channels showed a rise in TP concentrations in the water column in the dry season, reflecting higher aquatic productivity conditions and higher $TRIX_{PD}$ values. This was especially marked in the Igaraçu river. Even though the N:P ratio shows a limitation by nitrogen, the TP concentrations remained high in this season, with a mean of 0.18 mg L^{-1}. This may contribute to the maintenance of more elevated trophic states, as different groups of algae have different nutrient demands and some species are limited by P while others by N (Melo-Magalhães et al., 2016). Hydrochemical factors also contribute to these results, such as DO, D%O and Turbidity. According to Vollenweider et al. (1998), oxygen saturation (D%O) is a factor that expresses productivity-respiration in coastal waters, while a low turbidity may have an important influence on phytoplankton productivity due to the increased availability of photosynthetically active solar radiation in the euphotic zone.

During the rainy season, the Igaraçu river showed more elevated trophic conditions in all the sampling sites, with $TRIX_{PD}$ values ranging between 5 (Ig7) and 6.2 (Ig6). In the Parnaiba channel, the $TRIX_{PD}$ values ranged from 3.9 (P5) to 6.4 (P6 and P8), with an increasing trend along the estuarine gradient and with moderate productivity levels found in the mid estuary (P3 to P5). The reduced light penetration caused by the increased turbidity and TSS concentrations, a lower availability of TP in the water column, and the phosphorus limitation, expressed by the N:P ratio, seem to have a low impact on the reduction of the system's trophic level. Apparently, these conditions are offset by the conservative behavior of TN concentrations in the system. It is important to note that there is no direct relationship between the TRIX results and the N:P ratio, as the index alone does not make this kind of distinction (Vollenweider et al., 1998).

5. Conclusions

The hydrochemical variables pH, T, NTU, DO, D%O and TP showed a strong dependence on the intensity of the water flow, which modulated the water quality and the trophic behavior of the system. The use of probabilistic curves associated with multivariate analysis tools allowed for the best identification of the critical water quality variables and consequently showed the applicability of quality indices to the regional conditions of Northeastern Brazil. At the same time, the development and improvement of indices using a reduced number of variables are of great importance, especially for developing countries and regions where the costs involved in the analysis of certain parameters may limit the assessment of water quality.

The data shows a worsening of the water quality (WQI_{min}) when we compared the two seasons. In general, a lesser water quality is accompanied by an increase in the trophic level of the system. The sites downstream to Parnaíba City are strongly influenced by urban and industrial anthropogenic contributions, which demand control actions on the point sources of nutrients released to the estuary.

The use of WQI_{min} and TRIX_{PD} in the classification of fresh and brackish waters of the two deltaic channels is an attempt to apply water quality and trophic state assessment tools in the Brazilian northeastern coast. These indices allow us to survey the priority areas for the purposes of water pollution control, identifying portions of the estuary where the water quality is more degraded. This information allows for preventive and corrective actions to be taken by environmental agencies, thus contributing to the coastal management of the region.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

F.J. Paula Filho: Conceptualization, Writing - original draft. **R.V. Marins:** Resources, Supervision. **L. Chicharo:** Writing - review & editing. **R.B. Souza:** Formal analysis. **G.V. Santos:** Investigation. **E.M.A. Braz:** Methodology.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.rsma.2019.101025.

References

Alves, G., Flores-Montes, M., Gaspar, F., Gomes, J., Feitosa, F., 2013. Eutrophication and water quality in a tropical Brazilian estuary. In: Special Issue 65 - International Coastal Symposium. J. Coast. Res. 1 (65), 7–12. http://dx.doi.org/10.2112/SI65-002.1, Special Issue.

ANA - Agência Nacional de Águas, 2011. Guia nacional para coleta e preservação de amostras: água, sedimentos, comunidades aquáticas e efluentes líquidos. Compahia Ambiental do Estado de São Paulo, https://capacitacao.ana.gov.br/conhecerh/handle/ana/263, organizadores: Carlos Jesus Brandão et al., São Paulo: CETESB, Brasília, ANA.

ANA - Agência Nacional de Águas, 2012. Panorama da qualidade das águas superficiais no Brasil: 2012. Agência Nacional de Águas - ANA, Brasília, Avalilable in: http://www3ana.gov.br/portal/ANA.

Barroso, H.S, Becker, H., Melo, V.M.M., 2016. Influence of river discharge on phytoplankton structure and nutrient concentrations in four tropical semiarid estuaries. Braz. J. Oceanogr. 64 (1), 37–48. http://dx.doi.org/10.1590/S1679-87592016101406401.

Borsuk, M.E., Stow, C.A., K.H., Reckhow., 2002. Predicting the frequency of water quality standard violations: a probabilistic approach for TMDL development. Environ. Sci. Technol. 36 (10), 2109–2115. http://dx.doi.org/10.1021/es011246m.

BRASIL, 2005. Ministry of Environment. Brazilian National Council for the Environment. Resolution no 357. March 17. Available in: www.mma.gov.br/port/conama/res/res05/res35705.pdf. (Accessed 01 January 2018).

Bricker, S.B., Ferreira, J.G., Simas, T.C., 2003. An integrated methodology for assessment of estuarine trophic status. Ecol. Model. 169, 39–60. http://dx.doi.org/10.1016/S0304-3800(03)00199-6.

Burford, M.A., Rothlisberg, P.C., 1999. Factors limiting phytoplankton growth in a tropical continental shelf ecosystem. Estuar. Coast. Shelf Sci. 48 (5), 541–549. http://dx.doi.org/10.1006/ecss.1999.0471.

Caruso, G., Leonardi, M., Monticelli, L.S., Decembrini, F., Azzaro, F., Cdrisafi, E., Zappalá, G., Bermasco, A., Vizzini, S., 2010. Assessment of the ecological status of transitional waters in Sicily (Italy): First characterisation and classification according to a multiparametric approach. Mar. Pollut. Bull. 60, 1682–1690. http://dx.doi.org/10.1016/j.marpolbul.2010.06.047.

CETESB - Companhia Ambiental do Estado de São Paulo, 2018. Qualidade das águas interiores no estado de São Paulo 2017. CETESB, São Paulo, Available: https://cetesb.sp.gov.br/aguas-interiores/publicacoes-e-relatorios/.

Coelho, S., Gamito, S., Pérez-Ruzafa, A., 2007. Trophic state of Foz de Almargem coastal lagoon (Algarve, South Portugal) based on the water quality and the phytoplankton community. Estuar. Coast. Shelf Sci. 71, 218–231. http://dx.doi.org/10.1016/j.ecss.2006.07.017.

Cotovicz Junior, L.C., Brandini, N., Knoppers, B.A., Souza, W.F.L., Medeiros, P.R.P., 2012. Comparação de Modelos e Índices para Avaliação do Estado Trófico do Complexo Estuarino-Lagunar Mundaú-Manguaba, (AL). Geochem. Bras. 26 (1), 2–12. http://dx.doi.org/10.21715/gb.v26i1.353.

Cunha, D.G.F., Calijuri, M.C., 2010. Probabilistic analysis of the occurrence of incompatibility of the water quality with the legal framework of aquatic systems – case study of Pariquera-Açu River (SP Brazil). Eng. Sanit. Ambient. 15 (4), 337–346. http://dx.doi.org/10.1590/S1413-41522010000400006.

Cunha, D.G.F., Calijuri, M.C., Lamparelli, M.C., 2013. A trophic state index for tropical/subtropical reservoirs (TSI). Ecol. Eng. 60, 126–134. http://dx.doi.org/10.1016/j.ecoleng.2013.07.058.

Cunha, D.G.F., Calijuri, M.C., Mediondo, E.M., 2012. Integration between cumulative frequency curves for water quantity and quality as a tool for effective water resources management. Eng. Sanit. Ambient. 17 (4), 369–376. http://dx.doi.org/10.1590/S1413-41522012000400003.

Dabrowski, J., Bruton, S., Dent, M., Graham, M., Hill, T., Murray, K., Rivers-Moore, N., Van Deventer, H., 2013. Linking Land Use to Water Quality for Effective Water Resource and Ecosystem Management. WRC Report No. 1984/1/13, Water Research Commission, Pretoria, South Africa.

De Paula Filho, F.J., Marins, R.V., Lacerda, L.D., 2015a. Natural and anthropogenic emissions of N and P to the Parnaíba River Delta in NE Brazil. Estuar. Coast. Shelf Sci. 166 (Part A), 34–44. http://dx.doi.org/10.1016/j.ecss.2015.03.020.

De Paula Filho, F.J., Marins, R.V., Lacerda, L.D., Aguiar, J.E., Peres, T.F., 2015b. Background values for evaluation of heavy metal contamination in sediments in the Parnaíba River Delta estuary, NE/Brazil. Mar. Pollut. Bull. 91 (2), 424–428. http://dx.doi.org/10.1016/j.marpolbul.2014.08.022.

Devlin, M., Bricker, S., Painting, S., 2011. Comparison of five methods for assessing impacts of nutrient enrichment using estuarine case studies. Biogeochemistry 106 (2), 177–205. http://dx.doi.org/10.1007/s10533-011-9588-9.

Eschrique, S.A., 2011. Study of the Biogeochemical Balance of the Main Dissolved Nutrients as an Indicator of the Anthropic Influence in the Estuarine Systems of Northeast and Southeast Brazil (Ph.D. thesis). Oceanographic Institute, University of São Paulo, São Paulo, http://dx.doi.org/10.11606/T.21.2011.tde-19042012-151614.

Farias, A.C.S., Filho, A.A.F., Ivo, C.T.C., Fernandes, C.A.F., Cunha, F.E.A., 2015. Productive Chain of Fishing in the Interior of the Parnaíba Delta and Adjacent Marine Area. RDS, Fortaleza, p. 240, Available in: https://www.bdpa.cnptia.embrapa.br/consulta/busca?b=ad&id=1045292&biblioteca=vazio&busca=autoria:%22FERNANDES,%20C.%20A.%20F.%22&qFacets=autoria:%22FERNANDES,%20C.%20A.%20F.%22&sort=&paginacao=t&paginaAtual=1.

Figueiredo, J.A., Muniz, K., Macedo, S.J., Flores Montes, M.J., Feitosa, F.A.N., 2006. Hydrology and phytoplankton biomass in the Orange and Catuama (Santa Cruz channel) bars in Itamaracá-PE: nictemeral variation. Arq. Ciên. Mar. 39, 5–17, Available in: www.periodicos.ufc.br/arquivosdecienciadomar/article/view/6152.

Gopal, V., Shanmugasundaram, A., Nithya, B., Magesh, N.S., Jayaprakash, M., 2018. Water quality of the Uppanar estuary, Southern India: Implications on the level of dissolved nutrients and trace elements. Mar. Pollut. Bull. 130, 279–286. http://dx.doi.org/10.1016/j.marpolbul.2018.03.046.

Herrera-Silveira, J.A., Morales-Ojeda, S.M., 2009. Evaluation of the health status of a coastal ecosystem in southeast Mexico: assessment of water quality, phytoplankton and submerged aquatic vegetation. Mar. Pollut. Bull. 59, 72–86. http://dx.doi.org/10.1016/j.marpolbul.2008.11.017.

Knoppers, B.A., Souza, W.F.L., Ekau, W., Figueiredo, A.G., Soares-Gomes, A., 2009. A interface Terra- Mar do Brasil. In: R.C.C. Pereira and A. Soares-Gomes (Orgs.), Biologia Marinha, second ed. Interciência, Rio de Janeiro, pp. 529–553.

Lacerda, L.D., Molisani, M.M., Sena, D., Maia, L.P., 2008. Estimating the importance of natural and anthropogenic sources on N and P emission to estuaries along the Ceará State Coast NE Brazil. Environ. Monit. Assess. 141 (1), 149–164. http://dx.doi.org/10.1007/s10661-007-9884-y.

Luu, T.N.M., Garnier, J., Billen, G., Le, T.P.Q., Nemery, J., Orange, D., Le, L.A., 2012. N, P, Si budgets for the Red River Delta (Vietnam): how the delta affects river nutrient delivery to the sea. Biogeochemistry 107 (1–3), 241–259. http://dx.doi.org/10.1007/s10533-010-9549-8.

Marins, R.V., Lacerda, L.D., Abreu, L.M., Dias, F.J.S., 2003. Efeitos da açudagem no rio Jaguaribe. Ciên. Hoje 197 (33), 66–70.

Marins, R.V., Paula-Filho, F.J., Rocha, C.A.S., 2007. Phosphorus geochemistry as a proxy of environmental estuarine processes at the Jaguaribe river, northeastern Brazil. Quim. Nova 30, 1208–1214. http://dx.doi.org/10.1590/S0100-40422007000500029.

Marreto, R.N., Baumgarten, M.G.Z., Wallner-Kersanach, M., 2017. Trophic quality of waters in the Patos Lagoon estuary: a comparison between its margins and the port channel located in Rio Grande, RS, Brazil. Acta Limnol. Bras. 29, e11. http://dx.doi.org/10.1590/S2179-975X10716.

Medeiros, A.C., Faial, K.R.F., Faial, K.C.F., Lopes, I.D.S., Lima, M.O., Guimarães, R.M., Mendonça, N.M., 2017. Quality index of the surface water of Amazonian rivers in industrial areas in Pará, Brazil. Mar. Pollut. Bull. 123, 156–164. http://dx.doi.org/10.1016/j.marpolbul.2017.09.002.

Melo-Magalhães, E.M., Moura, A.N., Medeiros, P.R.P., Koening, M.L., 2016. Microphytoplankton biomass and trophic state of the Estuarine Region of São Francisco River (northeastern Brazil). Braz. J. Aquat. Sci. Technol. 20 (2), 51–62. http://dx.doi.org/10.14210/bjast.v20n2.5297.

Mitra, S., Ghosh, S., Satpathy, K.K., Bhattacharya, B.D., Sarkar, S.K., Mishra, P., Raja, P., 2018. Water quality assessment of the ecologically stressed Hooghly River Estuary, India: A multivariate approach. Mar. Pollut. Bull. 126, 592–599. http://dx.doi.org/10.1016/j.marpolbul.2017.09.053.

Molisani, M.M., Barroso, H.S., Becker, H., Moreira, M.O.P., Hijo, C.A.G., Monte, T.M., Vasconcellos, G.H., 2010. Trophic state, phytoplankton assemblages and limnological diagnosis of the Castanhão Reservoir, CE, Brazil. Acta Limnol. Bras. 22 (1), 1–12. http://dx.doi.org/10.4322/actalb.02201001.

Nascimento, F.C.R., Muniz, K., Feitosa, F.A.N., Araujo, J.P., Silva, R.M.S., Silva, G.S., Flores-Montes, M.J., 2003. Nutritional availability at Pina Basin and Tijipió River (Recife – PE – Brazil) in relation to nutrients and primary biomass (September/2000). Trop. Oceanogr. 30 (1), 97–117. http://dx.doi.org/10.5914/tropocean.v31i2.5023.

Noriega, C.D., Muniz, K., Feitosa, F.A.N., Flores Montes, M.J., Grego, C.K.S., Soares, G.S.S., Silva, H.F., 2005. Special distribution of phytoplankton biomass and its relationship with nutrient salts in the Barra das Jangadas estuarine system (Pernambuco-Brazil). Arq. Ciên. Mar. 38, 5–18. http://dx.doi.org/10.4236/oje.2017.77032.

O'Boyle, S., McDermott, G., Noklegaard, T., Wilkes, R., 2013. A simple index of trophic state in estuaries and coastal bays based on measurements of pH and dissolved oxygen. Estuaries Coast. 36 (1), 158–173. http://dx.doi.org/10.1007/s12237-012-9553-4.

Pereira, E.B., Martins, F.R., Abreu, S.L., Rüther, R., 2006. Atlas brasileiro de energia solar. INPE, São José dos Campos, p. 60, Available in: http://labren.ccst.inpe.br/atlas_2017html.

Pesce, S.F., Wunderlin, D.A., 2000. Use of water quality indices to verify the impact of Cordoba City (Argentina) on Suquia River. Water Res. 34, 2915–2926. http://dx.doi.org/10.1016/S0043-1354(00)00036-1.

Redfield, A.C., 1958. The biological control of chemical factors in the environment. Am. Sci. 46 (3), 205–221, https://www.jstor.org/stable/27827150.

Rocha, F.C., Andrade, E.M., Lopes, F.B., 2015. Water quality index calculated from biological, physicochemical attributes. Environ. Monit. Assess. 187, 1–15. http://dx.doi.org/10.1007/s10661-014-4163-1.

Rocha, F.C., Andrade, E.M., Lopes, F.B., de Paula Filho, F.J., Costa Filho, J.H., 2016. Physical-chemical determinant properties of biological communities in continental semi-arid waters. Environ. Monit. Assess. 188 (8), 489. http://dx.doi.org/10.1007/s10661-016-5497-7.

Silva, G.S., Jardim, W.F., 2006. A new Water Quality Index for protection of aquatic life appllied to the Atibaia river, region of Campinas/Paulínia cities – São Paulo State. Quím. Nova São Paulo 29 (4), 689–694. http://dx.doi.org/10.1590/S0100-40422006000400012.

Simões, F.S., Moreira, A.B., Bisinoti, M.C., Gimenez, S.M.N., Yabe, M.J.S., 2008. Water quality index as a simple indicator of aquaculture effects on aquatic bodies. Ecol. Indic. 8, 476–484. http://dx.doi.org/10.1016/j.ecolind.2007.05.002.

SNIRH. Sistema Nacional de Informações sobre Recursos Hídricos, 2018. Portal HidroWeb. http://www.snirh.gov.br/gestorpcd. (Accessed June 2018).

SNSA - Secretaria Nacional de Saneamento Ambiental, 2016. Sistema Nacional de Informações sobre Saneamento: diagnóstico dos serviços de água e esgoto. MCIDADES.SNSA, Brasília, Available in: http://www.snis.gov.br/diagnostico-agua-e-esgotos/diagnostico-ae-2016.

Strickland, J.D.H., Parsons, T.R., 1972. A practical handbook of sea water analysis. Bull. Fish. Res. Board Canada 167, 1–311, Available in: www.dfo-mpo.gc.ca/Library/1507pdf.

Sundareshwar, P.V., Morris, J.T., Koepfler, E.K., Fornwalt, B., 2003. Phosphorus limitation of coastal ecosystem processes. Science 299 (5606), 563–565. http://dx.doi.org/10.1126/science.1079100.

Tavares, J.L., Calado, A.L.A., Fontes, R.F.C., 2014. Initial studies to use the index TRIX for analysis of eutrophication in estuary Potengi river - Natal – RN – Brazil. Revista AIDIS de Ingeniería y Ciencias Ambientales: Investigación. Desarrollo Práct. 7 (3), 297–308, http://www.journals.unam.mx/index.php/aidis/article/view/46824.

Valderrama, J.C., 1981. The simultaneous analysis of total N and total P in natural waters. Mar. Chem. 10 (2), 109–122. http://dx.doi.org/10.1016/0304-4203(81)90027-X.

Vollenweider, R.A., Giovanardi, F., Montanardi, G., Rinald, A., 1998. Characterization of the trophic conditions of marine coastal waters with special reference to the NW Adriatic Sea: proposal for a trophic scale, turbidity and generalized water quality index. Environmetrics 9, 329–357. http://dx.doi.org/10.1002/(SICI)1099-095X(199805/06)9:3<329::AID-ENV308>3.0.CO;2-9.

WHO, 2008. Guidelines for Drinking Water Quality, third ed. Word Health Organization, Geneva, Recommendations, Vol. 1. Available: https://www.who.int/water_sanitation_health/publications/gdwq3rev/en/.

Wolanski, E., Chicharo, L., Alexandra Chicharo, M., Morais, P., 2006. An ecohydrology model of the Guadiana Estuary (South Portugal). Estuar. Coast. Shelf Sci. 70 (2006), 132–143. http://dx.doi.org/10.1016/j.ecss.2006.05.029.

Zhang, W., Arhonditsis, G.B., 2008. Predicting the frequency of water quality standard violations using Bayesian calibration of eutrophication models. J. Great Lakes Res. 34 (4), 698–720. http://dx.doi.org/10.3394/0380-1330-34.4.698.