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Revista Ibero-Americana de Ciências Ambientais
Ibero-American Journal of Environmental Sciences

Set 2022 - v.13 - n.9

RICA
REVISTA IBERO-AMERICANA DE CIÊNCIAS AMBIENTAIS

ISSN: **2179-6858**

This article is also available online at:
www.sustenere.co

Seasonal variability of water quality parameters in an urban tropical estuary (Northeast Brazil)

Tropical estuaries crossing urban areas are highly vulnerable to anthropogenic actions, mainly regarding eutrophication due to the excess of nutrients from domestic, urban, and industrial effluents. The present study assessed the interannual variability of physico-chemical parameters [salinity, pH, turbidity, temperature, dissolved oxygen, Biological Oxygen Demand - BOD, total ammoniacal nitrogen (NH3 + NH4+) - TAN, total phosphorus (dissolved + particulate) – T-P and true colour] in the Capibaribe River Estuary (northeast Brazil) over nine years at an upstream site (city suburbs) and a downstream site (downtown) representing the upper and middle estuary, respectively. The environmental variables differed significantly ($p < 0.05$), especially between seasons (dry and rainy) and sampling sites, as well as with season vs. site interactions. High concentrations of TAN (1.51 ± 2.54 mg L^{-1}) and TP (0.45 ± 0.32 mg L^{-1}) were recorded in the estuary. These concentrations, combined with high water temperatures (> 25 oC), contributed to scenarios of hypoxia and/or anoxia (23% of samples < 2 mg L^{-1}) that severely impair the conservation of aquatic life and even the value of urban landscape. The analysis of temporal and spatial trends in the variability of water quality parameters is of great importance for more critical decision-making processes regarding urban planning, water conservation measures within and around the estuary and for the recovery and maintenance of its ecological services.

Keywords: River basins; Anthropogenic actions; Environmental quality; Environmental variables.

Variabilidade sazonal dos parâmetros de qualidade da água em um estuário tropical urbano (Nordeste do Brasil)

Os estuários tropicais que atravessam áreas urbanas são altamente vulneráveis ??às ações antrópicas, principalmente no que diz respeito à eutrofização devido ao excesso de nutrientes provenientes de efluentes domésticos, urbanos e industriais. O presente estudo avaliou a variabilidade interanual dos parâmetros físico-químicos [salinidade, pH, turbidez, temperatura, oxigênio dissolvido, Demanda Biológica de Oxigênio - DBO, nitrogênio amoniacal total (NH3 + NH4+) - TAN, fósforo total (dissolvido + particulado) – T-P e true color] no estuário do Rio Capibaribe (Nordeste do Brasil) durante nove anos em um local a montante (subúrbios da cidade) e um local a jusante (centro) representando o alto e médio estuário, respectivamente. As variáveis ??ambientais diferiram significativamente ($p < 0,05$), principalmente entre as estações (seca e chuvosa) e locais de amostragem, bem como com as interações estação versus local. Altas concentrações de TAN (1,51 ± 2,54 mg L^{-1}) e TP (0,45 ± 0,32 mg L^{-1}) foram registradas no estuário. Estas concentrações, aliadas às altas temperaturas da água (> 25 oC), contribuíram para cenários de hipóxia e/ou anóxia (23% das amostras < 2 mg L^{-1}) que prejudicam gravemente a conservação da vida aquática e até mesmo o valor da paisagem urbana . A análise das tendências temporais e espaciais na variabilidade dos parâmetros de qualidade da água é de grande importância para processos de tomada de decisão mais críticos em matéria de planeamento urbano, medidas de conservação da água dentro e ao redor do estuário e para a recuperação e manutenção dos seus serviços ecológicos.

Palavras-chave: Bacias hidrográficas; Ações antropogênicas; Qualidade ambiental; Variáveis ambientais.

Topic: **Planejamento, Gestão e Políticas Públicas Ambientais**

Reviewed anonymously in the process of blind peer.

Received: **12/09/2022**
Approved: **28/09/2022**

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DOI: 10.6008/CBPC2179-6858.2022.009.0022

Referencing this:
NASCIMENTO, R. C. M.; COSTA, C. R.; CAVALCANTI, J. S. S.; COSTA, M. F.. Seasonal variability of water quality parameters in an urban tropical estuary (Northeast Brazil). **Revista Ibero Americana de Ciências Ambientais**, v.13, n.9, p.278-293, 2022. DOI: http://doi.org/10.6008/CBPC2179-6858.2022.009.0022

INTRODUCTION

Estuaries are acknowledged as highly complex environments exhibiting several ecological interactions (e.g. fish distribution) ruled by the fluctuations of water physico-chemical variables and biogeochemical processes (JAYACHANDRAN et al., 2012; RATNAYAKE et al., 2018; BARLETTA et al., 2019; MAMA et al., 2021; NASCIMENTO et al., 2021). Such processes are even more concerning in estuaries where, considering climatic conditions, high water temperature and excess organic loads from untreated effluents are present (RIBEIRO et al., 2016; HUERTA et al., 2019). Tropical estuaries have been constantly damaged due to the synergy of numerous anthropogenic impacts, which affect these ecosystems (SILVA et al., 2015; WENTZ et al., 2016; BI et al., 2017).

Domestic and industrial effluents are among the main impacts affecting estuaries, leading to increased loads of nutrients in the water column, mainly phosphorus and nitrogen forms (BARLETTA et al., 2009; BULL et al., 2021). High concentrations of these nutrients added to unplanned land use and occupation, inputs of domestic effluents often result in eutrophication (BRICKER et al., 2008), which in turn impairs environmental quality and ecosystem services (ALONGI, 2008; OELSNER et al., 2019). This is a worldwide concern (SHARPLEY et al., 2013), with a major expression in developing countries (CASSIDY et al., 2011, LANNERGARD et al., 2019), where excess nutrients are indicative of coastal waters degradation and even habitat loss (CARPENTER et al., 1998; BOYER et al., 2006; HOWARTH et al., 2011; OELSNER et al., 2019).

Nevertheless, estuaries are dynamic systems whose shifts in salinity, temperature, turbidity, and pH over spatial and temporal scales determine nutrient cycling and the availability of dissolved oxygen (GOMES et al., 2018; NORIEGA et al., 2022). For the maintenance of environmental quality in coastal systems it is asserted that significantly lowering pollution levels is the best approach to be considered globally (ARAÚJO et al., 2008; FARRELL et al., 2013). Therefore, water quality assessments are of great importance for scientific and managerial purposes, emphasizing that the monitoring of estuarine waters is extremely useful to describe and predict their behavior over space and time (ARAÚJO et al., 2008; RATNAYAKE et al., 2018).

The Capibaribe River Estuary is a tropical estuarine system in northeast Brazil that crosses a densely urbanized area (Recife City) (1.637.834 hab. in 7.557,41 km^2) (CPRH, 2012; IBGE, 2018) and should be playing a key role in environmental quality, including not only services to the city, but also the adjacent coastal area. However, for decades, it has been facing changes in water quality and sediment pollution resulting in the loss of native vegetation and fauna (MELO et al., 2018).

The present study identifies the seasonal changes in water quality of the Capibaribe River Estuary between 2004 and 2012 by (i) assessing the physic-chemical parameters over space and time, (ii) specially the temporal variations in the concentration of TAN and T-P in the water. The importance of the research lies in the long-term evaluation of physical-chemical variables in a tropical estuary with socio-environmental relevance. Understanding how the estuary behaved previously favors the projection of future models about water quality. Furthermore, analyzing water quality patterns on a time scale is an important basis for decision-making in the conservation of water and living resources.

MATERIALS AND METHODS

Study area

The Capibaribe River Estuary is in Recife city, State of Pernambuco (Fig. 1) where there is a tropically hot and humid climate according to Köppen (XAVIER et al., 2016), and exhibits well-defined dry (September to February) and rainy (March to August) seasons. The average total annual rainfall is ~2,200 mm and the average air temperature is ~25.2°C (OLIVEIRA et al., 2014).

The estuary is ~19 km long and 3 m deep on average (GASPAR et al., 2018). It is part of the Capibaribe river basin (7,454.88 km²) (LIMA et al., 2018). When it enters Recife at its suburbs, it presents a width of ~50 m in the upstream area and, downtown it is ~200 m wide, where its depth varies between 8 and 12 m (SCHETTINI et al., 2016a).

Anthropogenic modifications are observed across the entire river basin and estuarine course, manly regarding unplanned urban and industrial development (NASCIMENTO et al., 2021), as well as deforestation of the Atlantic Rain Forest and mangrove areas across the estuarine complex (XAVIER et al., 2016). Water from the river basin enters the estuarine course already compromised by a combination of factors among which agro-industrial, urban, and industrial effluents and irregular flow are the most important (AQUINO et al., 2014; SCHETTINI et al., 2016b).

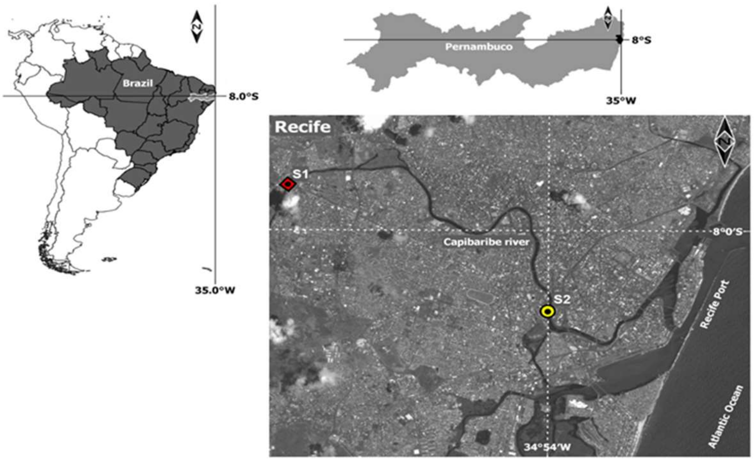

Figure 1: Geographic location of the Capibaribe River Estuary. S1 and S2 represents the upstream and downstream sites, respectively.

Data sources: Climatic and hydrological monitoring

The monitoring of water parameters within the Capibaribe River basin by CPRH began in 2001 and lasts until today. Two sampling sites within estuarine waters, S1 or upstream site (8°1'49.2587" S; 34°57'23.191" W) at Recife suburbs and S2 or downstream site (8°3'40.962" S; 34°54'1.137" W) downtown, set by the Pernambuco State Environmental Agency (Fig. 1), were chosen for this study. These sites are monitored according to their proximity to potential sources of pollution (CPRH, 2015). S1 lies at the head of the estuary and is where the river enters the city of Recife, by its suburban area. S2 is in the middle estuary, where tidal influence is already present, and contributes to dilution of riverine water as well as estuarine flush (SCHETTINI et al., 2016a).

Bimonthly monitoring of water quality parameters at these two sites has been done and made available online (CPRH, 2004; 2005; 2006; 2007; 2008; 2009; 2010; 2011; 2012). Therefore, at least three surveys per season [dry (February, October and December; and rainy (April, June, August)] are expected to be available. The samples were taken from sub-surface waters (1m depth) in the centre of the river channel (Fig. 2). Factors such as time of the day and tide were not accounted in the sampling design.

Monthly and historic data on total rainfall (mm) were compiled from the Climatic division of the Brazilian National Space Centre (CPTEC/INPE). The study region is under a meso-tidal regime (0 – 2.7m) (ARAÚJO et al., 2011), but this is expected to be less variable within the estuary. Previous studies have determined the reach of the tidal intrusion in this estuary and showed that at the upstream sampling station tide is dynamic, while at the downstream sampling station it results in variations of ~1.0m (SCHETTINI et al., 2016b).

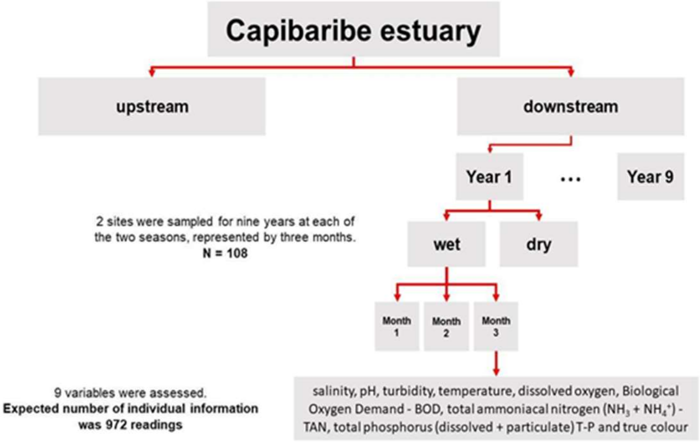

Figure 2: Sample design explaining the spatio-temporal approach used in the present work.

The physic-chemical parameters salinity, water temperature (°C), potential of hydrogen (pH), turbidity (NTU), dissolved oxygen (mg L^{-1}), biochemical oxygen demand (BOD) (mg L^{-1}), total ammoniacal nitrogen (TAN) (mg L^{-1}), total phosphorus (TP) (mg L^{-1}) and true colour (Pt/Co) were retrieved and compiled. All sampling procedures and analyses followed the methods proposed by the *American Public Health Association* (APHA, 1998; CPRH, 2004; 2005; 2006; 2007; 2008; 2009; 2010; 2011; 2012). The levels of TP, TAN, dissolved oxygen, turbidity, BOD, pH and colour measured in the estuary were compared to the suggested limits established for brackish water (proper for public supply after conventional treatment; conservation of aquatic communities and recreation) set by the National Council for the Environment (CONAMA n°357/05) and by the U.S. Environmental Protection Agency (US EPA 2015). A number of other studies have successfully used data from the same monitoring program at Capibaribe River Estuary and other estuaries of Pernambuco to model, explain and predict their water quality (e.g., COSTA et al., 2017; NORIEGA et al., 2013; CABRAL et al., 2019; GUNKEL et al., 2007).

Statistical analyses

All physico-chemical data was Box-Cox transformed for a better fit to a normal distribution (BOX et al., 1964). The Kolmogorov-Smirnov test and the histograms of dispersion for Gaussian curves were used to check the data homoscedasticity and normality, respectively (UNDERWOOD, 1997). Factorial analyses of variance (three way-ANOVA) were used to test whether each physico-chemical parameter (precipitation, salinity, water temperature, pH, turbidity, dissolved oxygen, BOD, turbidity, true colour, TAN and TP) differed among years, sites and seasonal periods. The Bonferroni's *post-hoc* test ($\alpha \leq 0.05$) was used whenever significant differences were detected (QUINN et al., 2002).

A Principal Component & Classification Analysis (PCCA) was used to compile the correlations between all physic-chemical parameters and categorical factors (year, season, and site) to verify the multidimensional influences of environmental variables on water quality. This analysis reduces the variables to highlight only the most representative and less correlated possible. Also, it checks for heterogeneity in relation to averages (±stdev). It analyses co-variances and correlations among variables simultaneously (JAMBU, 1991). All statistical analyses were performed using the STATISTICA® software, version 13.3.

RESULTS

The period from 2004 to 2012 was the best window of data in terms of amount (regularity in sampling) and quality (consistent set of parameters). Nine variables could be satisfactorily recovered, comprising 92.5% of the expected information. Results are expressed in seasonal averages (±stdev) for each sampling site (Fig. 3 and 4).

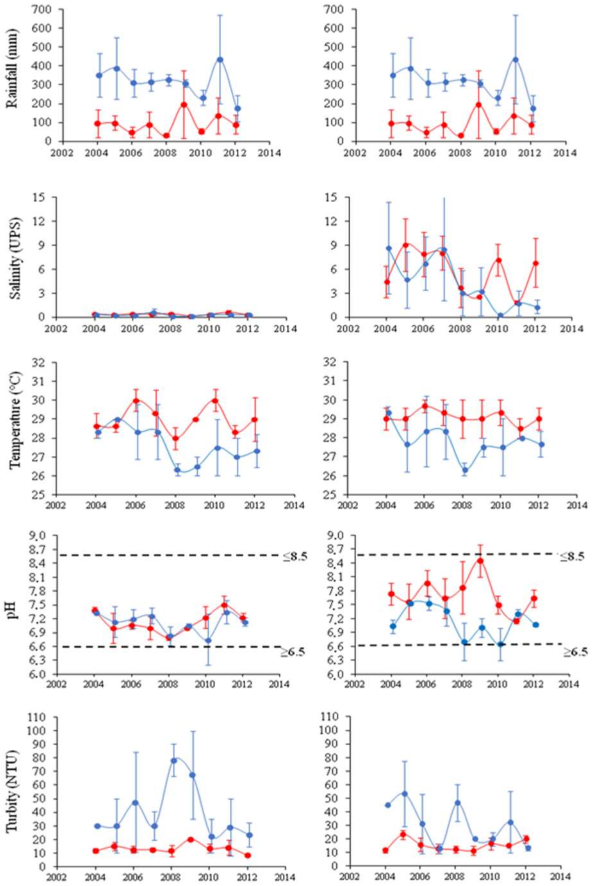

Figure 3: Interannual averages (±S.E.) of physico-chemical parameters during the dry (●) and rainy (●) seasons at the upstream and downstream sites. Black and grey dashed lines represent the limits required by Brazilian National Council for the Environment (CONAMA n°357/05) and the U.S. Environmental Protection Agency (EPA, 2015), respectively.

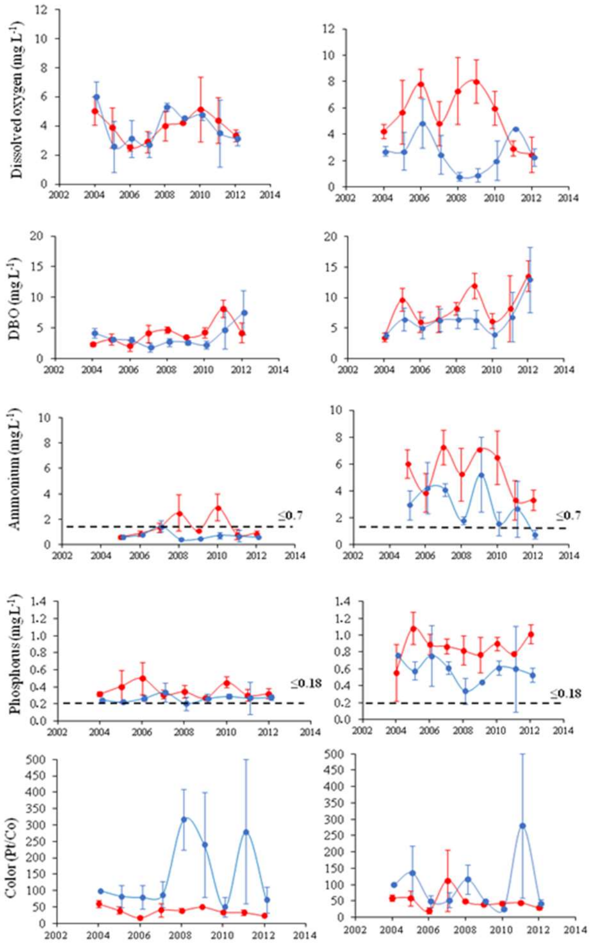

Figure 4: Interannual averages (±S.E.) of physico-chemical parameters during the dry (●) and rainy (●) seasons at the upstream and downstream sites. Black and grey dashed lines represent the limits required by the Brazilian National Council for the Environment (CONAMA n°357/05) and the U.S. Environmental Protection Agency (EPA, 2015), respectively.

Spatio-temporal variability of physico-chemical parameters

The precipitation was better explained by variations between the seasons ($p < 0.01$). Salinity and pH were better explained by variations between seasons and sites ($p < 0.01$); and by the season *vs*. site interactions ($p < 0.05$). The highest average values of salinity (1.85 ± 0.25 – 9.03 ± 3.29) and pH (7.15 ± 0.05 – 8.45 ± 0.35) were recorded at the downstream site during the dry season (Table 1).

Water temperature and turbidity were significantly explained by the variations between seasons ($p < 0.01$). The highest average values of water temperature (28.00 ± 0.58 – 30.00 ± 0.58°C) were recorded during the dry season, while the highest average values of turbidity (13.30 ± 1.67 – 78.33 ± 12.02 NTU) during the rainy season, regardless seasons and sites. Although not significant, the highest values of turbidity were observed at the upstream site (Table 1).

Dissolved oxygen was better explained by the variations between seasons ($p < 0.01$); and by the season *vs*. site interactions ($p < 0.01$). The lowest average values of dissolved oxygen (0.80 ± 0.21 – 4.83 ± 2.19 mg L^{-1}) were recorded during the rainy season at the downstream site. BOD was better explained by the variations among years and sites ($p < 0.01$). The highest average values of BOD were recorded in 2012 at the downstream site (dry: 13.60 ± 2.50 mg L^{-1}; rainy: 12.97 ± 5.34 mg L^{-1}) (Table 1).

TAN was better explained by the variations among years, seasons, and sites ($p < 0.05$). The highest average value of TAN (7.24 ± 1.28 mg L^{-1}) was observed during the dry season of 2012 at the downstream site ($p < 0.01$). TP was better explained by the variations between seasons and sites ($p < 0.01$). The highest average values of TP (0.56 ± 0.34 – 1.08 ± 0.19 mg L^{-1}) were observed during the dry season at the downstream site, regardless of years (Table 1).

True colour was better explained by the variation among years, seasons and sites ($p < 0.01$). The highest average value of true colour (316.67 ± 92.80 Pt/Co) was recorded during the rainy season of 2008 at the upstream site (Table 1).

Table 1: Results from the ANOVA for the average values of environmental variables. The differences observed among years, seasons and sites were determined by the Bonferroni's *post-hoc* test.

	Sources of variance			**Interactions**			
Variables	**Year (1)**	**Season (2)**	**Site (3)**	**1x2**	**1x3**	**2x3**	**1x2x3**
Salinity	ns	Dry Rainy**	S1 S2**	ns	ns	*	ns
Rainfall	ns	Dry Rainy**	ns	ns	ns	ns	ns
pH	ns	Dry Rainy**	S1 S2**	ns	ns	**	ns
Turbidity	ns	Dry Rainy**	ns	ns	ns	ns	ns
Temperature	ns	Dry Rainy**	ns	ns	ns	ns	ns
Dissolved Oxygen	ns	Dry Rainy**	ns	ns	ns	**	ns
BOD	04 06 07 10 05 08 09 11 12**	ns	S1 S2**	ns	ns	ns	ns
TAN	12 11 05 06 08 09 10 07*	Dry Rainy**	S1 S2**	ns	ns	ns	ns
TP	ns	Dry Rainy**	S1 S2**	ns	ns	ns	ns
Colour	06 12 10 07 05 09 11 04 08**	Dry Rainy**	S1 S2**	ns	ns	ns	ns

S1 – upstream, S2 – downstream; ns: not significant; *: p<0.05; **: p<0.01; underlined: homogeneous groups.

Relationship among environmental variables

To verify the relationships among physic-chemical variables and to isolate the variations caused by spatial and temporal changes in the Capibaribe River Estuary, a PCCA was used. The PCCA detected inter-relations among variables and isolated variations in physic-chemical variables in the Capibaribe estuary water quality along time and space that resulted from rainfall differences between seasons. According to the analysis, the two first factors (Factor 1 and 2) account for 69.93% of data variability (Fig. 5). The factor 1 explains 46.33% of the data and is mainly represented by the negative correlations with TP, TAN, salinity and water temperature (> 10% of variable contribution). The correlation between them is closely linked to contamination, in this case by excess nutrients, where both obtained high levels (Fig. 5). The factor 2 explains 23.60% of the data and is mainly represented by the positive correlations with true colour, turbidity, dissolved oxygen and pH (> 14% of variable contribution) (Fig. 5).

The factor year had a low power in the distribution of the data, whilst seasons and areas exhibited the greater influences, as shown by the length of the vectors. The first axis (factor 1) evidence strong positive relationships among TAN, TP, BOD, salinity and water temperature, emphasizing that increases in salinity and temperature are probably related to increases in nutrient input and increase the organic matter degradation. The second axis (factor 2) evidence that dissolved oxygen and pH have a positive relationship, with a direct effect on estuarine processes due to the availability of oxygen. The second axis also shows that turbidity and colour have a strong relationship with the rainy season, due to the increased concentrations of suspended solids flushed by the river discharge (Fig. 5).

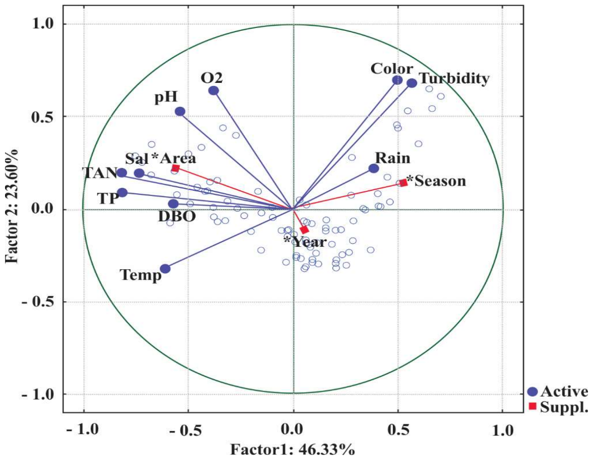

Figure 5: Biplot diagram of Principal Component & Classification Analysis (PCCA) displaying the environmental parameters (●) and categorical factors (■ - year, season and site) as vectors of active and supplementary variables, respectively, in the Capibaribe River Estuary from 2003 to 2012.

In the rainy season, with lower water temperatures, thus increasing the number of suspended particles available in the water body; the positive correlation between Dissolved Oxygen and pH indicates a direct relationship in estuary maintenance processes, either by oxygen availability or maintenance of chemical reactions (Table 2).

The negative correlation between Dissolved Oxygen and temperature is given by the fact that oxygen decreases with increasing temperature. In addition, the anti-correlation of the nutrients TAN and TP with Dissolved Oxygen and BOD is a eutrophication factor in the estuary, causing the concentration of organic matter to be higher, consequently increasing the demand for oxygen (Table 2). Precipitation, colour, and turbidity showed no negative correlations with any of the variables (Table 2).

Table 2: Summary of Principal Component & Classification Analysis (PCCA) with the contributions (%) and correlations between the physico-chemical parameters and the first two ordination axes; and the total variance explained.

	Variable contribution (%)		**Factor *vs.* variable correlations**	
Variables	**Factor 1**	**Factor 2**	**Factor 1**	**Factor 2**
Active				
Dissolved Oxygen	0.039	0.192	-0.380	0.596
BOD	0.081	0.005	-0.545	0.097
TAN	0.168	0.037	-0.786	0.262
TP	0.169	0.014	-0.787	0.159
Colour	0.074	0.244	0.520	0.671
Salinity	0.136	0.032	-0.706	0.242
Rainfall	0.053	0.036	0.439	0.258
Temperature	0.108	0.051	-0.629	-0.307
pH	0.075	0.148	-0.523	0.524
Turbidity	0.098	0.241	0.601	0.667
Supplementary				
*Year	-	-	0.035	-0.117
*Season	-	-	0.530	0.181
*Site	-	-	-0.530	0.301
	Eigenvalue	**%Total Variance**		
Factor 1	3.669	46.33		
Factor 2	1.846	23.60		

DISCUSSION

The monitoring of estuarine environmental quality through a set of physic-chemical parameters compiled into a consistent matrix can help to understand changes occurring in the system and allows the data to be compared with other sites (NASCIMENTO et al., 2018). These physic-chemical parameters play a fundamental role in environmental diagnosis aimed at diverse ends (conservation, public supply) (WANG et al., 2019).

Salinity, in average, showed higher concentrations at the downstream site, closer to the estuary mouth and the sea. Seasonal variation in rainfall results in increased river flow during the rainy season, which dilutes the salt water. On the other hand, saline intrusion is favoured during the dryer periods (REUM et al., 2014). The salinity variability is also influenced by the tidal cycle on a daily timescale (semi-diurnal meso-tides of approx. 2.7m) (SCHETTINI et al., 2016b; LIU et al., 2021). The saline intrusion could favour dilution of pollutants load during the dry season only at the downstream site, when riverine flux is reduced. This process counterbalances the high nutrients load that reaches the estuary at this time of the year.

Tropical estuaries are susceptible to extreme variability in abiotic parameters, especially those relative to the seasonal fluctuation of salinity influenced by changes in river discharge during dry and rainy periods (CARVALHO et al., 2011). These systems present seasons with high and constantly high-water temperatures due to the climate (COSTA et al., 2017). Such characteristics are of fundamental importance for the local biota (SEEKEL et al., 2013). Water temperatures influence the structure of faunal communities, physiological rates and animal activities (TRONQUART et al., 2013); and determine environmental quality (HARRISON et al., 2006).

Most values of pH are within the limits required for freshwater set by the local (CONAMA, 2005) and North American legislation (U.S. EPA), for example, that suggest values in the ranges of 6.0 to 9.0 and 6.5 to 8.5, respectively (Table 3). Turbidity and colour are parameters strongly influenced by rainfall. Higher values of these two parameters are expected during rainy months, when the suspended solids increase in the water body. In addition, estuarine turbidity and colour are related to tidal intrusion (NAVRATIL et al., 2011).

Table 3: Limits for water quality parameters in freshwater and brackish water set by the Brazilian National Council for the Environment (CONAMA) and the U.S. Environmental Protection Agency (EPA) and the percentage of samples outside these limits for both upstream and downstream sites.

Parameter	CONAMA	% above limit	EPA	% above limit
Dissolved O_2 (mg L^{-1})	-	-	-	-
TAN (mg L^{-1})	≤ 0.7	100	-	-
TP (mg L^{-1})	≤ 0.18	100	-	-
Colour (Pt/Co)	-	-	-	-
Turbidity	-	-	-	-

In the present study, the sample with turbidity of 120 NTU found in June 2006 at the upstream site and the sample with 100 NTU found in June 2005 at the downstream site corroborated with the observations expected in the literature, indicating periods of very high turbidity. On the other hand, the colour index exceeded the limits for freshwaters set by the Brazilian national agency (≤ 75 Pt/Co), and the limits established by US-EPA (≤ 15 Pt/Co). Although colorimetric indexes are not causally linked to the loss of water quality, indexes above the advised might be an alert and the investigation of other water parameters is necessary.

Hypoxic and anoxic conditions

The low oxygen availability in coastal areas is a major concern worldwide (COSTA et al., 2017; 2018). Low oxygen levels (≤ 2 mg L^{-1}) may occur naturally due to factors such as climate, stratification of the water column, biological processes, among others. However, anthropogenic activities relative to uncontrolled and unregulated disposal of nutrient-rich effluents are often the main causes of hypoxic conditions (GOODMAN et al., 2007). In addition, physic-chemical and hydrodynamic factors that tend to decrease the dilution capacity of estuaries increase oxygen stress (BARLETTA et al., 2017; 2019; COSTA et al., 2016). To degrade the excess organic matter in the Capibaribe River Estuary, microorganisms use dissolved oxygen (SILVA et al., 2016), thus, the BOD levels also tend to increase in the system. Prolonged periods with oxygen levels below 2 mg L^{-1}; limited water circulation and exchange, stratification and a high CO_2 export to the atmosphere are characteristic of hypoxia. The ration between primary production and CO_2 concentration increases respiration. Another determining factor is nutrient load that tends to increase with population growth (RABALAIS et al., 2010).

Hypoxic conditions were frequent during the dry seasons because of the low rainfall rates and low capacity of water renewal, leading to the entrapment of nutrients within the estuary (BAIRD et al., 2004). The exposition of the estuary to high loads of nutrients resulted in levels of dissolved oxygen ≤ 2 mg L^{-1}, or below, at both sites and seasons, with a higher number of records found during the rainy seasons. Anoxic conditions were also noticed, characterizing the estuary as particularly vulnerable (EKSTROM et al., 2015). Unfortunately, episodes of anoxia and hypoxia are increasingly present in the oceans and estuaries (DIAZ et al., 2008; NASCIMENTO et al., 2020) and are generally observed during periods of drought due to the limited water circulation and estuarine flux (KIM et al., 2014; 2018; LEE et al., 2018). The eutrophication of Capibaribe River Estuary is observed in both seasonal periods and does not represent a consistent pattern. Moreover, the events of hypoxia and anoxia recorded in the estuary are related to a larger discharge of effluents and urban runoff (LAMARDO et al., 2016).

Concentration of nutrients

The Capibaribe River Estuary exhibited high concentrations of dissolved nutrients over the nine years of study. The load of nutrients has a great influence in the eutrophication status and, consequently, in the low (or wide oscillating) levels of dissolved oxygen observed in the system (Table 3). These modifications have a direct influence on the local fauna, such as noticed by the significant losses of, for example, fishes' diversity and surrounding mangrove areas in recent years (LAMARDO et al., 2016; MELO et al., 2018).

Newton et al. (2003) used DPSIR to assess eutrophication in Ria Formosa (Portugal), and report that under different legislation the same site can have different water quality status, since some have different tolerance levels. This analysis can also highlight the contribution of factors as basic sanitation, wastewater treatment, agricultural runoff and other inputs Eutrophication can also be explained by variables as tidal amplitude, depth, water temperature, salinity, distance to the sea, turbidity, and not necessarily by nutrients concentrations (HUGUES et al., 2011; CLOERN, 2001).

The concentration of total phosphorus (TP) is known as an accelerator of eutrophication processes in tropical and sub-tropical waters, limiting the growth of many species (SHARPLEY et al., 2001; BOOMER et al., 2012). Controversially to the eutrophication reported in the present study, Silva et al. (2016) observed a significant increase of species of the fauna and flora at the downstream site of the estuary due to a strong influence of the ocean. This is interesting because the monitoring of water parameters over a decade revealed that the greatest values of phosphorus were observed at the upstream site. Although not accounting for a community approach, the local environmental conditions do not favour such development.

Eutrophication indexes require the composition of variables as Chlorophyll- a that were not available for the period considered (VONLLENWEIDER et al., 1998). Bricker et al. (2008) studied estuaries in North America and showed that land use and trophic state are closely correlated. In practically half of the cases studied, eutrophication resulted from sewage, and was expressed by the presence of aquatic macrophytes, among other bioindicators. When analysing results from four transects regarding trophic state, chlorophyll-a and N:P, a high concentration of NH_4^+ was observed corresponding to domestic sewage inputs without treatment. Nutrients were inversely correlated to salinity and a suggestion of nutrient use by primary producers as the water approached the end of the estuary (BRANDINI et al., 2016). TAN is a good indicator of nitrogen species and water quality. The greater concentrations of TAN were recorded during the dry season. During the rainy season and high tides, TAN is diluted (CHESTER, 2000). In the Capibaribe River Estuary, such dilution is not satisfactorily completed due to the extremely high concentration of ammonium, which reached 9.79 mg L^{-1} at the downstream site in December 2007, for example. In addition, the levels of TAN and TP were often above the levels required for freshwater and brackish water set by the national and North American legislations (Tables 1 and 2), regardless of year, season, and site.

The nutrient input into the system is likely associated to the presence of 65 industries with pollution potential in areas close to the estuary, the improper use and occupation of soils and 150 wastewater disposal sites, including untreated domestic effluents (CPRH, 2007; LAMARDO et al., 2016). Despite knowledge about this contamination observed in recent years, there was no significant improvement in the managerial or environmental situation (BRAYNER et al., 2003; GUENTHER et al., 2015; 2019; SCHETTINI et al., 2016a).

Some studies reported greater compromising of water quality when near agricultural areas (low oxygen levels and high nutrients concentration), as well as poorly sanitised areas, from where wastewaters flow directly into the river. Better water quality could be detected in the middle of the main channel, away from the margins. Also, wind speed, rainfall, and depth contributed to this improvement (CABRAL et al., 2019).

Coastal regions are increasingly suffering from the presence of stressors linked to human actions, most of which affect biodiversity and ecosystem functioning (MICHELI et al. 2016). Such vulnerability compromises resilience of estuaries and resulting poor environmental quality (WORM et al., 2006, HALPERN et al., 2008), as observed in the studied estuary. The environmental agency has recently adjusted its set of monitored parameters and their sampling frequency. Water quality at these sites is now monitored every three months (February, May, August, and November), and now calculates the Trophic State Index for the upstream site. Results also point towards permanent eutrophication. Additionally, the Capibaribe River Estuary is responsible for net emissions of CO_2 into the atmosphere varying from 30 to 48 mmol m^{-2} day^{-1} (NORIEGA et al., 2013; GASPAR et al., 2018), also being an altered source of nitrogen and phosphorus for adjacent coastal waters (CPRH, 2017). The results of this study also suggest the estuary as a source of CO_2 (NORIEGA et al., 2013; GASPAR et al., 2018). Therefore, actions aiming at recovering the health of this ecosystem requires preventive measures, including restoration of its margins, but above all basic sanitation (sewage and urban runoff). Then, it will be possible to significantly reduce the amount of nutrients entering the estuary and assist in its environmental restoration.

CONCLUSIONS

The analysis of the water quality in the Capibaribe River Estuary through the physico-chemical data from the Pernambuco State Environmental Agency monitoring program demonstrated that high contents of TP and TAN occurred during all nine years studied, independent of season. The concentration of nutrients often exceeded those recommended by the relevant national and international parameters due to direct inputs to the river, severely affecting environmental quality, and possibly biodiversity of the estuary and adjacent systems. The results indicated that eutrophication processes vary seasonally, with tendencies of increase during dry periods. In addition, we suggest the high nutrient loads are related to anoxia and hypoxia episodes. Since 2012, urban population has increased in number and density without the necessary infra-structure to match. Water quality is then expected to have worsened since the last year included in this study, reducing the overall quality of the urban environment as well as the water exported to coastal waters. This is an impairment to the objectives of water conservation and, ultimately, the expectations of better living conditions to the local population and visitors.

Unless the sampling design is improved (more sites, higher frequency, and more representative set of parameters) and rigorously followed (no gaps), the presently available and future data might not be sufficient to improve this type of analysis. This is a concern, since Recife is undergoing intense and irreversible changes driven by land-based, climatic and oceanographic variables. Its geography is, on average, vulnerable to floods, storms and tides, which challenges estuarine water renewal and resilience.

The above mentioned recommendations may assist in a better informed and more responsible decision-making processes by the local government and environmental agencies concerned estuarine and coastal conservation.

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