

Alkalinity, inorganic carbon and CO₂ flux variability during extreme rainfall years (2010-2011) in two polluted tropical estuaries NE Brazil

Felipe Lima Gaspar^{1*}, Barbara Ramos Pinheiro¹, Carlos Esteban Delgado Noriega¹, Moacyr Araujo¹, Nathalie Lefèvre¹, Manuel de Jesus Flores Montes¹

¹ Laboratório de Oceanografia Química da Universidade Federal de Pernambuco
(Av. da Arquitetura s/n - Recife - PE 50740540 - PE)

*Corresponding author: figaspar@gmail.com

ABSTRACT

The susceptibility of coastal environments to shifts in the biogeochemical cycles of carbon and nutrients driven by anthropogenic pressure and climate change is a real challenge for the scientific community. This paper evaluated the effects of an extreme rainfall event over the nutrients and carbonate parameters in two polluted tropical estuaries. Surface water samples were taken seasonally along a salinity gradient in the Capibaribe and Barra de Jangadas estuaries in order to investigate the spatial and seasonal variability of dissolved nutrients, chlorophyll-*a*, dissolved oxygen, total alkalinity, inorganic carbon, partial pressure of CO₂ (pCO₂) and CO₂ fluxes. The increased riverine influence caused by the fluvial flooding during the extremely rainy season augmented the nitrogen concentrations in the plumes, which also presented reduced salinity, alkalinity and dissolved oxygen values. In the Capibaribe plume it has also shifted the mean CO₂ flux value of - 4.01 mmolC m⁻² d⁻¹ during the dry season, to a positive mean flux of + 5.7 mmolC m⁻² d⁻¹ during the rainy season. Within the estuaries the BOD_{5,20} and dissolved phosphorus values were higher during the dry season ($p < 0.0001$), they showed positive correlation with the phytoplanktonic blooms that reached a chl-*a* value of 85 mg m⁻³ in the Capibaribe. The high alkalinity found in both estuaries, with mean values between dry and wet seasons respectively from 1808 to 1373 μmol kg⁻¹ in the Capibaribe estuary and 1616 to 1058 μmol kg⁻¹ in Barra de Jangadas estuary, may act as a buffer to the process of coastal acidification due to eutrophication. The increased rivers discharge lead to a greater transport of organic matter and nutrients to the coast, decreasing the oxygen availability and shifting the metabolic status of the estuarine plume to heterotrophic, whereas increased the water quality within the estuaries due the flushing promoted by the extreme rainfall event.

Descriptors: Anthropogenic pollution, Ocean acidification, Eutrophication, Extreme event.

RESUMO

A suscetibilidade dos ambientes costeiros às mudanças nos ciclos biogeoquímicos do carbono e nutrientes impulsionados pela pressão antrópica e mudanças climáticas é um verdadeiro desafio para a comunidade científica. Este artigo avaliou os efeitos de um evento de precipitação extrema sobre os parâmetros de oxigênio, nutrientes e do sistema carbonato em dois estuários tropicais poluídos. As amostras de água superficial foram retiradas sazonalmente ao longo de um gradiente de salinidade nos estuários do Capibaribe e Barra de Jangadas, a fim de investigar a variabilidade espacial e sazonal dos nutrientes dissolvidos, clorofila-*a*, oxigênio dissolvido, alcalinidade total, carbono inorgânico, pressão parcial de CO₂ (pCO₂) e fluxos de CO₂. O aumento da influência ribeirinha causada pelas inundações fluviais durante a estação de precipitação extrema aumentou as concentrações de nitrogênio nas plumas dos estuários, que também apresentaram valores reduzidos de salinidade, alcalinidade e oxigênio dissolvido. Na pluma do Capibaribe o valor médio de fluxo de CO₂ também mudou, passou de - 4,01 mmolC m⁻² d⁻¹ durante a estação seca, para um fluxo médio positivo de + 5,7 mmolC m⁻² d⁻¹ durante a estação chuvosa. Dentro dos estuários, os valores de BOD_{5,20} e fósforo dissolvido foram maiores durante a estação seca ($p < 0,0001$) e apresentaram correlação positiva com os *blooms* fitoplanctônicos que atingiram um valor de chl-*a* de 85 mg m⁻³ no Capibaribe. A alta alcalinidade encontrada em ambos os estuários, com valores médios entre estações seca e chuvosa, respectivamente, de 1808 a 1373 μmol kg⁻¹ no estuário Capibaribe e 1616 a 1058 μmol kg⁻¹ no estuário Barra de Jangadas, pode atuar como um amortecedor para o processo de acidificação costeira devido à eutrofização. O aumento da descarga dos rios levou a um maior transporte de matéria orgânica e nutrientes para o litoral, diminuindo a disponibilidade de oxigênio e deslocando o estado metabólico da pluma estuarina para heterotrófico, enquanto aumentou a qualidade da água dentro dos estuários devido ao aumento de descarga promovido pela precipitação extrema.

Descritores: Poluição antrópica, Acidificação marinha, Eutrofização, Evento extremo.

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INTRODUCTION

Estuaries play an essential role in the transportation to and transformation of carbon of continental and atmospheric origin in the ocean (Sabine et al., 2004; Chen, 2004; Flores Montes et al., 2011; Travassos et al., 2016; Guenther et al., 2015). Some studies have shown that changes in land use and land cover in river basins can alter the natural balance of bicarbonate ions and contribute to alkalinity inputs into estuaries (Cai and Wang, 1998; Wang and Cai, 2004). However, the effect of the allochthonous and autochthonous inputs on the balance of alkalinity and nutrients in estuaries remains uncertain (Flores Montes et al., 2011). This may affect the magnitude of the capture/emission of CO₂ and lead to changes in the natural balance of production and mineralization of organic matter remains uncertain (Borges, 2011).

The focus of recent studies of inorganic carbon dynamics are the large rivers and estuaries, especially in mid and high latitudes, despite the significant contribution of small tropical rivers and estuaries, which together cover an area larger than the temperate estuaries (orges). As a result of limited data from tropical regions, current estimates of the global average flux of CO₂ are biased (Cai, 2011). Moreover, the CO₂ flux to the atmosphere depends on the calculation of the exchange rate *k*, which shows great variability related to local environmental features such as tide, depth, direction and wind intensity (Raymond and Cole, 2001; Abril and Borges, 2005; Borges et al., 2004).

Anthropogenic pressure adds various stressors such as pollution, overfishing, changes in the land use and cover, amongst others to the coastal environments. These impacts are expected to increase in the future with continued changes in the global climate system and increases in human population levels (Howard et al., 2013). According to Trenberth (2011), it is expected that the effect of climate change on winds and precipitation may be moderate, but will vary regionally. Consequently, these climate change effects may alter the magnitude of the CO₂ fluxes at the air/water interface and the water residence time in estuaries, which is an important factor in the regulation of alkalinity in estuarine environments (Cai, 2011).

The Brazilian coast extends for over 8000 km and is home to 50.7 million people, equivalent to 26.6% of the country's population (IBGE, 2010). Population growth in the coastal region has led to an increase in nutrient export to the coast, due to the release of untreated sewage into rivers and estuaries (Noriega and Araujo, 2009).

According to Noriega et al. (2013) the estimated average flux for the Capibaribe estuary ranges from 10.95 to 17.52 molCO₂ m⁻² y⁻¹ during high tide in a regular rainfall year. Those authors also reported the average emissions of ~0.35 Tg C y⁻¹ for estuaries in the Brazilian Northeast.

In the present study, we analyzed the seasonal and spatial distribution of nutrients, alkalinity, dissolved inorganic carbon, and pCO₂ and CO₂ fluxes in two estuaries located in areas of high population density during a seasonal cycle of extremely heavy rainfall using measurements of total alkalinity, pH, temperature, salinity, dissolved inorganic nitrogen, total phosphorus (TP) and silicate.

METHODS

STUDY SITE

There are three major rivers in the Recife Metropolitan Region (RMR), which are Capibaribe, Jaboatão and Pirapama, whose waters are used for public water supply and the disposal of industrial effluents and domestic sewage without appropriate treatment. The land use activity in these watersheds is primarily urban and industrial, including areas of sugarcane monoculture, and some vestigial areas of Atlantic Forest and mangrove forest (CPRH, 2011). Several studies have identified an increase in nutrient concentrations, human eutrophication and algal blooms in this region in recent years (Travassos et al., 1993; Koenig et al., 1995; Feitosa et al., 1999; Noriega and Araujo, 2009; Noriega and Araujo, 2011; Flores Montes et al., 2011; Guenther et al., 2015) and organic pollution (Paulo et al., 2011; Travassos et al., 2016).

The Capibaribe River watershed covers a drainage area of ≈7,557 km² and is used by a population of approximately 1,328,361 inhabitants (CPRH, 2011). The Capibaribe estuary has a mean depth of 3m and an approximate area of ≈19 km² located entirely within the city of Recife.

The estuarine area of the Barra de Jangadas (BJ) is formed by the confluence of the Jaboatão and Pirapama rivers, which together drain an area of approximately 1,022 km² and whose waters are used by a population of approximately 1,347,053 inhabitants (CPRH, 2011). This estuary, covering approximately 14 km², and has an average depth of 2.6 m and a variable width of approximately 150 m.

Both river basins are located within the geological Formation called "Tabuleiros Costeiros do Nordeste", characterized by Tertiary and Quaternary sediments which

forms coastal plains constituted by sandy soils closer to the coast and inland there are the occurrence of yellow-red latosols and podsols, moreover small stretches of alluvial eutrophic soils along river valleys (Silva, 1995).

The river flows are intermittent in the inner semi-arid portions of the Pernambuco state depending on the amount of rainfall, but are permanent where they flow into the Atlantic Ocean. The estuaries located in the RMR come under a semidiurnal tidal regime with present mean ranges of 1.3 m during the neap tide and 1.8 m during spring tide (Araujo et al., 1999).

SAMPLING

The estuaries were divided into different segments according to the longitudinal saline gradient classification proposed by McLusky (1992). The upper estuary was defined as the area where salinities are <2.5 , the medium estuary $2.5 < S \leq 30$ and the upper estuary $S > 30$. Six sampling campaigns were performed bimonthly between November 2010 and September 2011 at 12 stations distributed across the Capibaribe estuary and 11 stations in the Barra de Jangadas estuary (Fig. 1). There were also four sampling stations located within each estuarine plume.

The samples were taken from the surface layer during the low-water spring tide to assess the influence of the riverine and urban inputs to the coastal areas. The water samples were collected with Niskin oceanographic bottles and sent to the Laboratory of Chemical Oceanography and the Primary Productivity Lab, at the Federal University of Pernambuco (UFPE) where they were processed and analyzed.

Temperature and salinity were determined in situ with a CTD SBE19. pH was measured on board with a Ross combination electrode, measured on the total scale with a precision of ± 0.01 units and accuracy of 0.1%.

The monthly meteorological data of precipitation, air temperature, atmospheric pressure and wind speed at 10m above sea surface were obtained from the Pernambuco Agency of Water and Climate (APAC) and the National Institute of Meteorology (INMET). River discharge data were obtained from the National Water Agency (ANA).

ANALYSES

Dissolved oxygen (DO) was determined using the modified Winkler method (Strickland and Parsons, 1972) with an accuracy of $\pm 1.3 \mu\text{mol.L}^{-1}$. Oxygen saturation was

calculated using temperature and salinity data, in accordance with Garcia and Gordon (1992).

Samples for the analysis of the biological oxygen demand (BOD) were collected in accordance with the recommendations described in Standard Methods - APHA (1995), and incubated for five days at 20°C ($\text{BOD}_{5,20}$).

The alkalinity was determined in unfiltered water samples by potentiometric titration with H_2SO_4 0.016 mol L^{-1} as described in Radtke et al. (2012) with a precision of $15 \mu\text{mol kg}^{-1}$ and an accuracy of 2%.

The samples for determination of total dissolved phosphorus (TDP) precision $0.1 \mu\text{mol kg}^{-1}$, and accuracy of 1%, dissolved reactive silicate $\text{Si}(\text{OH})_4$ precision $1 \mu\text{mol kg}^{-1}$ and accuracy 2%, dissolved inorganic nitrogen (DIN), which is the sum of ammonia-N - ($\text{NH}_4^+ + \text{NH}_3$) precision $0.1 \mu\text{mol kg}^{-1}$ and accuracy 2%, nitrite (NO_2^-) precision $0.1 \mu\text{mol kg}^{-1}$ and accuracy 1%; and nitrate (NO_3^-) precision $0.5 \mu\text{mol kg}^{-1}$ and accuracy 1%, were analyzed by the methods described in Grasshoff et al. (1983) and are expressed in $\mu\text{mol kg}^{-1}$. The method for determining phytoplankton biomass (Chl-*a*) was the spectrophotometric analysis described in UNESCO (1966).

CALCULATIONS

Carbon dioxide solubility in the water was calculated in accordance with Weiss (1974). Total inorganic carbon $\text{TCO}_2 = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$ and the partial pressure of CO_2 ($p\text{CO}_2$) were calculated with the CO_2calc software, developed by Robbins et al. (2010), using alkalinity, pH, temperature, salinity, TP and reactive silica data. We used the dissociation constants of carbonic acid in accordance with Millero et al. (2006), and the dissociation constants of borate and sulfate given, respectively, by Dickson (1990a) and Dickson (1990b).

CO_2 flux was calculated as follows:

$$F(\text{CO}_2) = k(\text{CO}_2) \cdot K_H^{\text{CO}_2} \cdot \Delta p\text{CO}_2 \quad (\text{Eq. 1})$$

Where $F(\text{CO}_2)$ is the air/water flux of CO_2 ($\text{mmol m}^{-2} \text{d}^{-1}$), $k(\text{CO}_2)$ is the transfer velocity of CO_2 , $K_H^{\text{CO}_2}$ is the solubility of CO_2 (Weiss, 1974) and $\Delta p\text{CO}_2$ is the difference of $p\text{CO}_2$ between surface water and the atmosphere. Positive values indicate outgassing towards the atmosphere.

The $p\text{CO}_2$ in the atmosphere was calculated as follows:

$$p\text{CO}_{2\text{atm}} = x\text{CO}_{2\text{atm}} \cdot (P_{\text{atm}} - p\text{H}_2\text{O}) \quad (\text{Eq. 2})$$

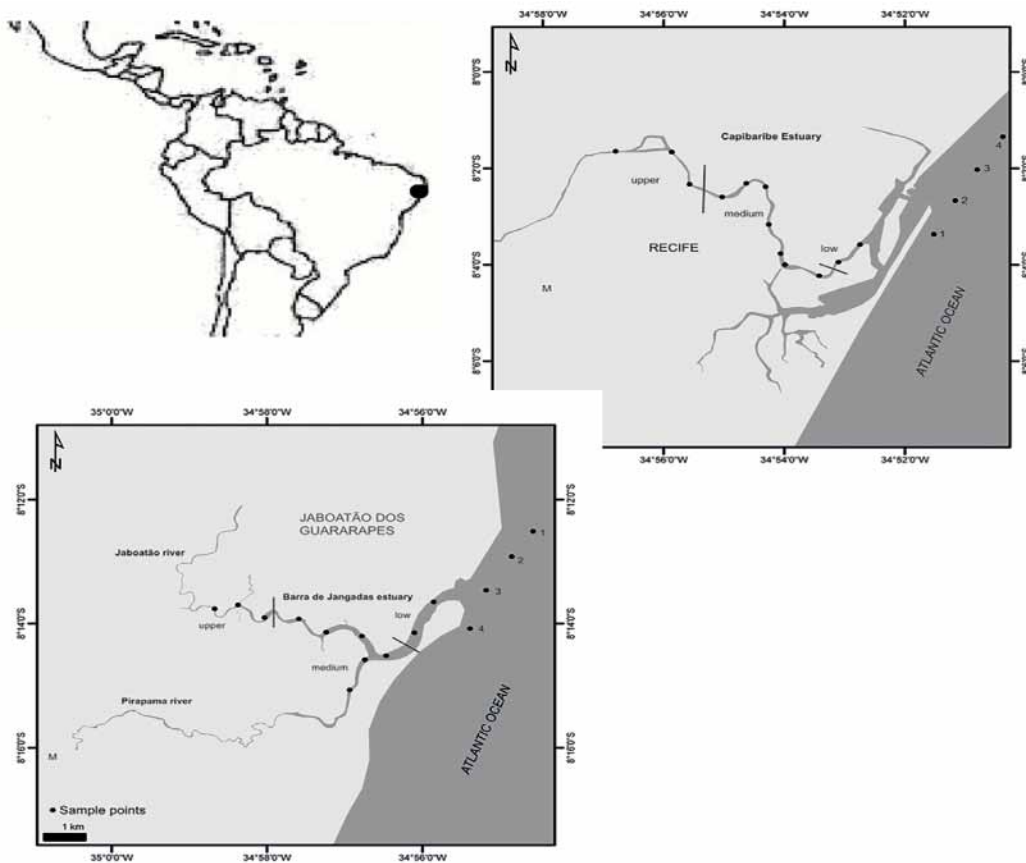


Figure 1. Map of the study area with the respective sampling stations. The numbers indicate the river plume stations. The M indicates the meteorological stations at which the precipitation, evaporation and wind speed data were recorded.

Where P_{atm} is the atmospheric pressure and xCO_{2atm} is the molar concentration of CO_2 in dry air in parts per million, obtained from the NOAA station located in Maxaranguape, 330 km north of Recife. Finally pH_2O is the vapor pressure of water at the sea surface.

The gas transfer velocity $k(CO_2)$ was calculated using the formula of Raymond and Cole (2001):

$$K(CO_2) = 1,51 \cdot \exp(0,35(u)) \cdot (Sc/600)^{-0,5} \quad (\text{Eq. 3})$$

Where u ($m \cdot s^{-1}$) is the mean wind speed 10 m above the sea surface on the sampling campaign day, and Sc is the Schmidt number in salt water for the CO_2 , calculated as a function of temperature.

An empirical model developed by Cole and Cloern (1987) for estimating phytoplankton productivity in the coastal areas was used. The above authors found a mean coefficient of determination $r^2=0.82$ using nine data sets and a highly

significant relationship ($p<0.001$) between production and B , Z_p , and I for the pooled data ($n=211$) given by:

$$P(\text{mmol Cm}^{-2} \text{d}^{-1}) = B \times Z_p \times I \quad (\text{Eq. 4})$$

where B represents the phytoplankton biomass (mg m^{-3} of chlorophyll- a), Z_p is the photic depth in meters (measured by Secchi disk), and I is the surface irradiance.

The depth limit of the photic layer (Z_p), which receives 1% of the radiation that reaches the surface, was calculated using the equation $Z_p=4.61/k$ proposed by Cole and Cloern (1987), where k is the coefficient of light attenuation calculated using the depth of disappearance of the Secchi disk (Z_{ds}), ($k=1,7/Z_{ds}$) as described by Poole and Atkins (1929).

The radiometric irradiance data used to calculate productivity were obtained from the Center for Weather Forecasting and Climate Studies/National Institute for Space Research - CPTEC/INPE, available at www.cptec.br.

inpe.br. These data were converted to photosynthetically active radiation (PAR - cal.g. cm².d⁻¹) by applying the correction factor of 0.47, as described by Vollenweider (1974). Values of PAR were converted into values of quantum E (m² d⁻¹) using a correction factor of 0.192, as described by Colijn (1982).

The seasonal water and salt flux average budgets for each estuary were calculated according to Gordon et al. (1996) and the residence time we calculated by equation 5.

$$\tau = Vol_{\text{estuary}} / (V_x | V_R) \quad (\text{Eq.5})$$

STATISTICS

The data normality was tested using the Shapiro-Wilks test. We used the t-test to compare the historical means with the 2010/2011 monthly means of precipitation and wind velocities, with a significance level $\alpha=0.05$. Since some of the variables didn't showed a normal distribution due to a reduced data pool, we used the Kruskal-Wallis test, with a level of significance $\alpha=0.05$ to identify whether there were seasonal and/or spatial differences in the pooled data.

In order to examine the links between all the variables measured, a principal component analysis (PCA) was used. Linear regressions and Pearson's correlations were calculated to assess variables distributions along the salinity gradient and under different rivers discharge conditions.

RESULTS

CLIMATOLOGY AND RIVER DISCHARGE

The average air temperature ranged between 23.71°C and 27.91°C. The mean wind speed for the area was 1.82 m s⁻¹, varying between 0.6 and 2.86 m s⁻¹. These values are close to the average wind speed for 1990-2010 of 2.2 m s⁻¹.

During the period from 2010 to 2011, the rainfall was above the expected values for some months of the rainy season (April to July), relative to the climatological average registered for 1990 to 2010 (Fig. 2 B, D). There was no significant difference in annual precipitation (t-test, $p=0.3149$), only in the monthly distribution of the rainfall as shown by the t test (t-test, $p=0.017$). The river discharge values for the Capibaribe (37.7 m³ s⁻¹) and Pirapama (20.7 m³ s⁻¹) found during this study were higher than the averages calculated from data provided by the Brazilian National Water Agency (Fig. 2 A, C).

The mixing flow (V_x) in the Capibaribe estuary was always below the residual flow (V_r), while the opposite dynamic was observed at the Barra de Jangadas estuary (Table 1). This latter act as an importer of salt, particulate and dissolved material while the Capibaribe estuary act as an exporter to the coastal zone. The residence time during the extreme rainfall event decreased ≈ 3.5 times and ≈ 10 times in the Capibaribe and Barra de Jangadas estuaries respectively.

DISSOLVED OXYGEN

Seasonally, the maximum dissolved oxygen values registered in the Capibaribe estuary were found during the rainy season (Kruskal-Wallis, $p<0.0001$ between seasons). During the dry season, in November 2010 and September 2011, the oxygen values found in this estuary increased during phytoplanktonic blooms. No seasonal variability was identified for this parameter in the Barra de Jangadas estuary with low values throughout the study (Figure 3).

The highest dissolved oxygen saturations (%DO) were found in the estuarine plumes, with annual mean values \pm sd of 98 \pm 10% and 86 \pm 14% for Barra de Jangadas and Capibaribe, respectively. A seasonal difference was identified only in the BJ plume, where the mean %DO decreased from 104% during the dry season to 88% (Kruskal-Wallis, $p=0.0024$) during the rainy season (Table 2).

The most extreme variability of the %DO was found in the Capibaribe estuary. The spatial distribution pattern of the %DO tended to decrease toward the lower estuary, with an annual mean value \pm standard deviation (sd) of 74 \pm 33% in the upper estuary and 29 \pm 34% in the lower estuary, where anoxic conditions were not rare. In Barra de Jangadas, the maximum %DO annual average was found at the low estuary 50 \pm 20%, decreasing towards the upper estuary (14.8 \pm 8.7%), and resulting in an average overall oxygen saturation below 30% throughout the study period.

The Capibaribe estuary showed an annual average BOD_{5,20} of 5.6 mg l⁻¹, three times higher than the mean found for the BJ estuary (1.82 mg l⁻¹). There was no clear variability linked to seasonal cycles. Spatially, most of the high values were found within the estuaries (Table 2) but these values showed no correlation with salinity (Figure 3).

DIN, TP, SILICATE AND CHL-*a*

The results of dissolved inorganic nutrients are presented in Table 2 for estuaries and Table 3 for the estuarine

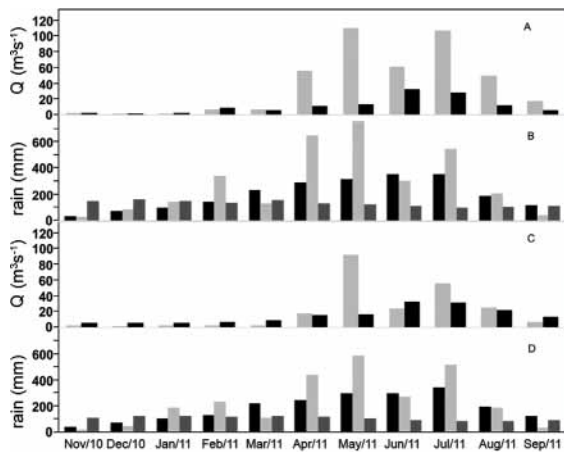


Figure 2. River discharge (gray) and mean discharge (black) from 1986 to 2009 in the Capibaribe (A) and from 1990 to 2009 in Barra de Jangadas (C). Monthly precipitation in the cities of Recife (B) and Jaboatão (D), monthly precipitation (gray), Thornthwaite's potential evapotranspiration (dark gray), average precipitation from 1990 to 2010 (black). There was no difference in annual rainfall (*t-test* $p > 0.05$) only in the monthly precipitation distribution (*t-test* $p = 0.017$).

Tabela 1. Seasonal water and salt flux average budgets for each estuary. Vq river discharge; Vp precipitation; Ve evaporation; Vr residual flow; Soc ocean salinity; Ssys river salinity; Sr residual salinity; Vx mixing flux; t residence time do bod x sal

	Capibaribe		Barra de Jangadas	
	dry	wet	dry	wet
Vq ($10^3 \text{ m}^3 \text{ d}^{-1}$)	778	9374	280	6350
Vp ($10^3 \text{ m}^3 \text{ d}^{-1}$)	10	151	5	103
Ve ($10^3 \text{ m}^3 \text{ d}^{-1}$)	17	34	12	23
Vr ($10^3 \text{ m}^3 \text{ d}^{-1}$)	-771	-9491	-273	-6430
Soc	34	22	35.5	23
Ssys	2.5	0.3	8.4	1
Sr	22.5	11.15	25.25	12
Vx ($10^3 \text{ m}^3 \text{ d}^{-1}$)	754	4877	336	3507
t (days)	25	7	43	4

plumes. The Capibaribe estuary and its plume showed the highest average concentrations of all nutrients. In this estuary, dissolved inorganic nitrogen (DIN) was negatively correlated with salinity, decreasing seaward ($r^2=0.69$). No correlation between these parameters was identified in the Barra de Jangadas estuary (Figure 4). The mean values of DIN showed a significant difference between rainy and dry seasons only within the Capibaribe estuary ($p < 0.0001$). The annual overall average DIN concentrations were $22.5 \pm 7.34 \mu\text{mol kg}^{-1}$ for the Capibaribe and $12.9 \pm 7.65 \mu\text{mol kg}^{-1}$ for the Barra de Jangadas estuary.

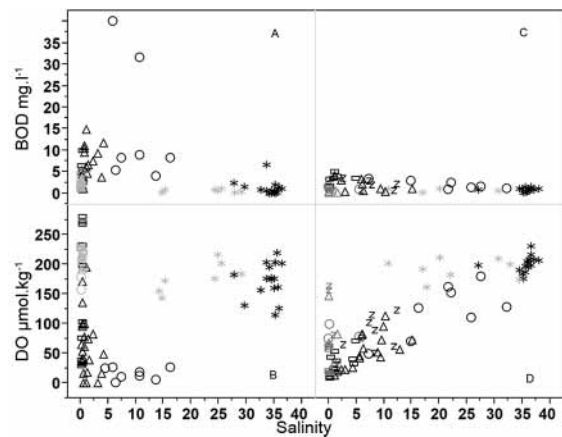


Figure 3. Overall distribution of the BOD and OD for the Capibaribe (A, B) and Barra de Jangadas (C, D) (black=dry season; gray = rainy season). *estuarine plume; circles - lower estuary; triangles - middle estuary; rectangles -upper estuary; z Pirapama.

The estuarine plumes showed a clear correlation between DIN and rainfall $r^2=0.60$ and 0.78 for the Capibaribe and Barra de Jangadas plumes, respectively. Through a seasonal comparison of DIN, we found p values of 0.0011 and 0.0006 for the BJ and Capibaribe plumes respectively. The increased riverine influence caused by the fluvial flooding during the extremely rainy season augmented the DIN concentrations in the plumes (Table 3), as was also seen by the salinity decrease.

The total dissolved phosphorus (TDP) maximum values were found during the dry season in both estuaries ($p=0.0191$) for Barra de Jangadas and ($p < 0.0001$) for the Capibaribe estuary. The mean overall TDP concentrations found within the BJ and Capibaribe estuaries were $3.53 \pm 2.11 \mu\text{mol kg}^{-1}$ and $7.18 \pm 4.51 \mu\text{mol kg}^{-1}$, respectively.

Seasonally, there were significant variations in the silicate concentrations (Table 2) in the Capibaribe estuary ($p=0.0289$) and in the plumes of the Capibaribe ($p=0.0001$) and BJ ($p=0.0041$). The mean \pm sd concentrations increased from $5.98 \pm 4.74 \mu\text{mol kg}^{-1}$ in the dry season to $48.11 \pm 37.31 \mu\text{mol kg}^{-1}$ in the rainy season in the BJ plume. In the Capibaribe plume the mean values ranged from $11.8 \pm 11.15 \mu\text{mol kg}^{-1}$ in the dry season to $64.44 \pm 21.05 \mu\text{mol kg}^{-1}$ during the rainy season ($p=0.0001$).

The phytoplanktonic biomass within the estuaries is shown in Figures 5 A and 5 B. There was no correlation between rainfall and chl-*a* in the Barra de Jangadas estuary ($r^2=0.01$). In the Capibaribe estuary the average chl-*a* concentration was higher during the dry season,

Tabela 2. Seasonal mean, minimum and maximum values of the parameters measured in the Capibaribe and Barra de Jangadas estuaries

		ESTUARY			
		Capibaribe		BJ	
		dry	wet	dry	wet
%DO	Mean	32.5	83.1	29.9	28.1
	Min - max	0 - 116	63 - 94	3.4 - 85	6.2 - 65
	n	42	24	40	19
BOD mg l ⁻¹	Mean	7.87	2.61	2.22	0.84
	Min - max	0.7 - 39.9	0.92 - 4.55	0.42 - 5.03	0.09 - 1.5
	n	33	25	28	11
DIN μmol kg ⁻¹	Mean	20.0	26.6	12.7	13.4
	Min - max	3.8 - 37.7	15.3 - 39.3	3.3 - 39.8	8.3 - 17.5
	n	42	24	40	19
TDP μmol kg ⁻¹	Mean	8.8	4.4	4.7	2.3
	Min - max	1.5 - 22	2.9 - 8.6	0.67 - 30.7	1.29 - 3.22
	n	42	24	40	19
Si(OH) ₄ μmol kg ⁻¹	Mean	108.9	131.1	89.0	102.6
	Min - max	10.5 - 207.3	38.5 - 209.5	10.17 - 194.3	38.73 - 195.5
	n	42	24	40	19
chl- <i>a</i> mg m ³	Mean	40.23	6.31	5.72	4.81
	Min - max	10 - 85	3.81 - 10.48	0.6 - 34.7	1.03 - 8.02
	n	14	8	16	5
TA μmol kg ⁻¹	Mean	1808	1373	1616	1058
	Min - max	1307 - 2421	973 - 1859	746 - 2090	622 - 1388
	n	42	24	40	19
pH	Mean	7.34	7.43	7.21	6.67
	Min - max	7.01 - 8.09	7.2 - 7.62	6.78 - 7.98	6.39 - 6.91
	n	42	24	40	19

influenced by the recurrent algal blooms, and resulted in a negative correlation between rainfall and chl-*a* $r^2=0.50$ with a significant seasonal difference ($p=0.0002$). During the campaigns, it was possible to identify an algal bloom event in November 2010 in both estuaries, when the chl-*a* values reached the maximum values of 85.11 mg m⁻³ in the Capibaribe, and 34.71 mg m⁻³ in the BJ estuary. A second bloom event was registered in September 2011, though less intense and only in the Capibaribe estuary, where the chl-*a* values ranged from a minimum of 22.94 mg m⁻³ to a maximum of 50.34 mg m⁻³. In the estuarine plumes (Figures 5 C, D) the chlorophyll *a* was lower than in the estuaries throughout the year and showed only a significant seasonal variation in the Capibaribe plume due to the algal blooms ($p=0.0011$).

TOTAL ALKALINITY, TCO₂, pH

The spatial variability of total alkalinity (TA) and pH are shown in Figure 6. Within the estuaries the alkalinity increases towards the lower estuary as a result of greater seawater influence. A positive correlation between TA and salinity was weak in the Capibaribe estuary $r^2=0.42$, but the correlation between these parameters was more evident in the BJ estuary $r^2=0.62$ (Figure 6 A, C).

It was found a significant seasonal and spatial differences in the TA values ($p<0.0001$ and $p=0.0278$, respectively), total alkalinity was higher in the Capibaribe estuary, with an annual average of 1649±390 μmol kg⁻¹, ranging from 1557±315 μmol kg⁻¹ in the upper estuary to 1860±49 μmol kg⁻¹ in the lower estuary. For the Barra de Jangadas estuary, the annual average alkalinity was

Tabela 3. Seasonal mean, minimum and maximum values of the parameters measured in the Capibaribe and Barra de Jangadas estuarine plumes

		PLUME			
		Capibaribe		BJ	
		dry	wet	dry	wet
%DO	Mean	88.5	83.0	104.1	88.8
	Min - max	60 - 114	63- 101	91 - 119	72 - 101
	n	16	8	15	8
BOD mg l ⁻¹	Mean	1.17	0.58	0.89	0.66
	Min - max	0.01 - 6.6	0.12 - 1.15	0.14 - 1.5	0.12 - 1
	n	16	7	15	4
DIN μmol kg ⁻¹	Mean	3.7	14.8	1.5	4.6
	Min - max	ND - 12	8.3 - 21.6	ND - 9.59	2.1 - 7.61
	n	16	8	15	8
TP μmol kg ⁻¹	Mean	2.4	3.5	1.9	1.8
	Min - max	ND - 9.75	2.22 - 5.09	0.5 - 5.1	0.8 - 2.9
	n	16	8	15	8
Si(OH) ₄ μmol kg ⁻¹	Mean	11.1	64.4	9.7	48.1
	Min - max	1 - 41.5	42.7 - 113.6	0.8 - 61.8	6.3 - 107
	n	16	8	15	8
chl- <i>a</i> mg m ³	Mean	4.99	2.35	3.24	1.54
	Min - max	0.24 - 19.29	1.15 - 3.93	0.21 - 9.67	0.8 - 2.49
	n	16	8	16	8
TA μmol kg ⁻¹	Mean	2266	2067	2262	1904
	Min - max	2094 - 2499	1721 - 2433	2038 - 2383	1250 - 2266
	n	16	8	15	8
pH	Mean	8.13	7.83	8.17	8.01
	Min - max	7.97 - 8.32	7.31 - 8.17	7.96 - 8.28	7.76 - 8.21
	n	16	8	15	8

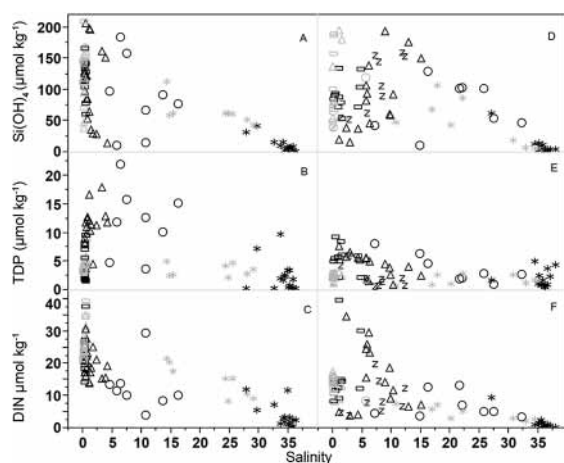


Figure 4. Overall distribution of the dissolved nutrients along the salinity gradient in the estuaries of the Capibaribe (A,B,C) and Barra de Jangadas (D,E,F), (black = dry season; gray = rainy season). *river plume; circle - lower estuary; triangle - middle estuary; rectangle - upper estuary; z - Pirapama.

1430±375 μmol kg⁻¹ and ranged from 1138±288 μmol kg⁻¹ in the upper estuary to 1668±361 μmol kg⁻¹ in the lower estuary.

The lowest average alkalinities were recorded during the rainy season in both estuaries (Table 2), with means±sd for this season of 1078±244 and 1372±375 μmol kg⁻¹ in the BJ and Capibaribe estuaries, respectively. There was no significant difference in TA between river plumes, with an annual average of 2142±308 μmol kg⁻¹ in the BJ and 2196±198 μmol kg⁻¹ in the Capibaribe.

With regard to pH, both estuaries showed a positive correlation with salinity, r²=0.62 and 0.79 for the Capibaribe and Barra de Jangadas, respectively (Figure 6 B, D). Average pH values within the BJ estuary were lower during the rainy months (6.70±0.21) and higher in the dry season (7.21±0.32). For the Capibaribe estuary, the pH values varied seasonally with mean ± sd for the rainy and dry seasons of 7.42±0.11 and 7.33 ± 0.23 (Table 2).

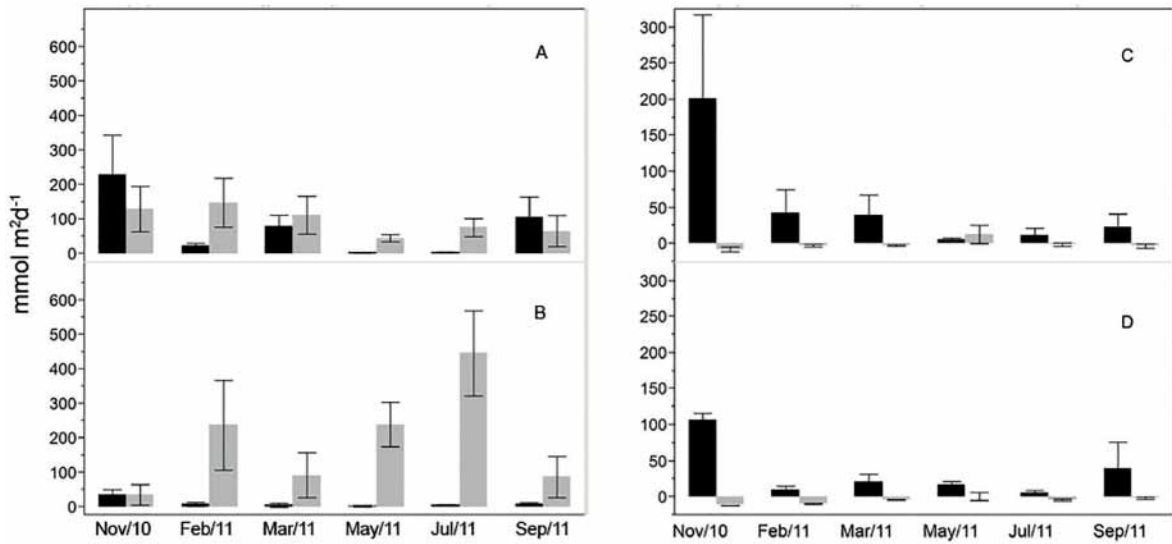


Figure 5. Monthly variability of the CO₂ fluxes (gray) and primary productivity (black) within the estuaries of the Capibaribe (A) and Barra de Jangadas (B), and in the river plumes (C), (D). Error bars represents standard deviation.

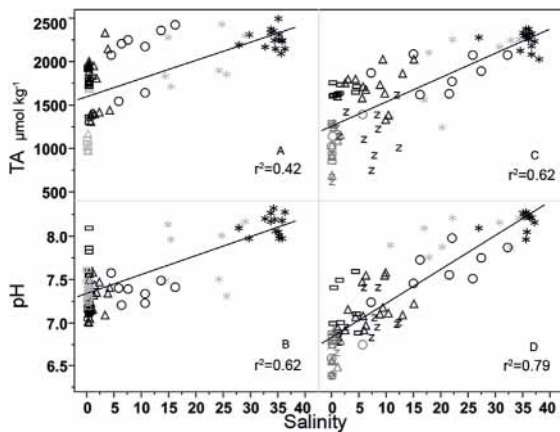


Figure 6. Overall distribution along a salinity gradient of total alkalinity (TA) and pH in the estuaries of the Capibaribe (A,B) and Barra de Jangadas (C,D) (black=dry season; gray=rainy season). *river plume; circle - lower estuary; triangle - middle estuary; rectangle - upper estuary; z Pirapama).

The pH values also varied seasonally in both river plumes, with the lowest values recorded during the rainy season for the Capibaribe ($p=0.0372$) and Barra de Jangadas ($p=0.0301$) (Table 3).

The PCA was used here to determine the influence of the pluviometry on the chemical parameters measured over time and space scales. There is a clear difference between dry and rainy period (Figure 7) where was found more elevated values of DIN, silicate in the estuaries and in the river plumes. The phytoplanktonic blooms events which

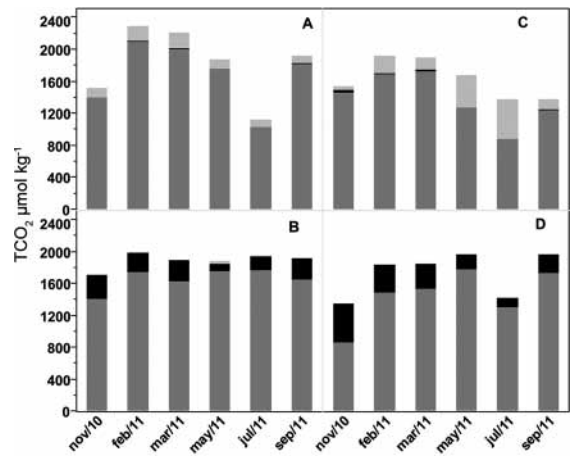


Figure 7. Principal component analysis obtained from the observed data in the Capibaribe (open markers) and Barra de Jangadas (solid markers). The numbers in F1 and F2 axis labels are the explained variance in each factor. (black=dry season; gray=rainy season). *river plume Capibaribe; Y river plume BJ; circle - lower estuary; triangle - middle estuary; rectangle - upper estuary; z Pirapama).

occurred during the dry period were linked to the elevated TDP and BOD_{5,20} values, thus the %DO increased in the rainy season in response to the decrease in the organic load in the estuaries (Figure 7).

During the dry season the lower estuary station in BJ is grouped with the estuarine plume (Figure 7A) it changes in the rainy season due the increased influence of freshwater promoted by the extreme rainfall. Such event led to a

decrease in the salinity of the river plumes and decreased the differences among river plume and lower estuary, especially in the Capibaribe (Figure 7).

The TCO_2 was also higher in the Capibaribe than in BJ ($p=0.0027$), with annual averages of $1764\pm 407 \mu\text{mol kg}^{-1}$ and $1638\pm 306 \mu\text{mol kg}^{-1}$, respectively. Variations in TCO_2 values accompanied the variation in alkalinity and were lower during the rainy season in both estuaries. The maximum relative HCO_3^- contributions to TCO_2 were registered in the Capibaribe estuary with a mean \pm sd of $91\pm 3.68\%$ of the TCO_2 composed by HCO_3^- (Figure 8).

Although the TCO_2 did not show any seasonal variation in the river plumes, the relative contribution of inorganic carbon species varied, with a decrease in the percentage of CO_3^{2-} ions and a relative increase of HCO_3^- ions and $\text{CO}_{2(\text{aq})}$ (Figure 8), accompanied by a pH decrease during the high discharge months of April and May 2011.

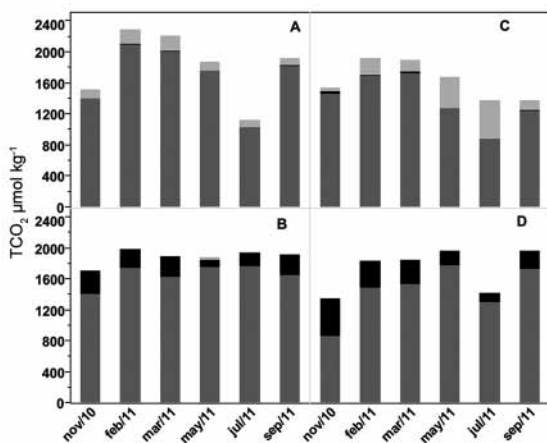


Figure 8. Monthly variability of the mean inorganic carbon species to TCO_2 within the estuaries of the Capibaribe (A), Barra de Jangadas (C), and in the river plumes of the (B) Capibaribe, and (D) Barra de Jangadas. (dark gray - $[\text{HCO}_3^-]$, Black - $[\text{CO}_3^{2-}]$, light gray - $[\text{CO}_2]$).

WATER pCO_2 AND CO_2 FLUXES

The estuaries showed a different seasonal pattern in the partial pressure of CO_2 (pCO_2) and CO_2 fluxes (FCO_2), for each estuary. The pCO_2 and the FCO_2 were higher during the rainy season in the Barra de Jangadas estuary and during the dry season in the Capibaribe estuary (Figures 5 and 8).

In the estuarine plumes, values of TA, pH and salinity were lower during the rainy season, increasing the pCO_2 , with mean values \pm sd of $667\pm 537 \mu\text{atm}$ in the Capibaribe

and $332\pm 189 \mu\text{atm}$ in the BJ (Figure 8 B). During the dry season the mean pCO_2 values found were $237\pm 86 \mu\text{atm}$ and $166\pm 112 \mu\text{atm}$ for the estuarine plumes of the Capibaribe ($p=0.0110$) and Barra de Jangadas ($p=0.0131$), respectively.

The maximum pCO_2 values were registered in the upper estuary, with low salinity, pH and alkalinity, mainly in the Barra de Jangadas estuary and decreased seawards $r^2=0.53$ (Figure 9 D). A significant correlation was not found in the Capibaribe estuary $r^2=0.36$ (Figure 9 B). The annual overall mean pCO_2 in the Capibaribe estuary was $3317\pm 2034 \mu\text{atm}$, ranging from $3142\pm 2282 \mu\text{atm}$ in the upper estuary to $2316\pm 710 \mu\text{atm}$ in the lower estuary. In Barra de Jangadas the annual overall pCO_2 mean was $6018\pm 4589 \mu\text{atm}$, with average values \pm sd ranging from $7852\pm 4308 \mu\text{atm}$ in the upper estuary to $3533\pm 4615 \mu\text{atm}$ in the lower estuary, where CO_2 subsaturation states were frequent during the dry season.

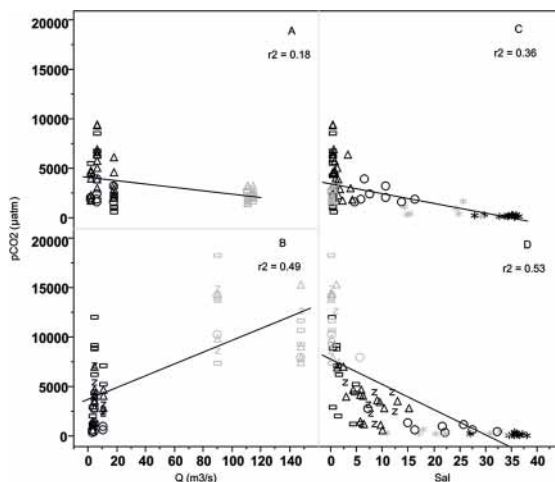


Figure 9. Correlation between river discharge (Q) and pCO_2 within the Capibaribe (A); and Barra de Jangadas (B) estuaries. Overall distribution of pCO_2 in the Capibaribe (C), and Barra de Jangadas (D), along a salinity gradient (black = dry season; gray = rainy season). *river plume; circle - lower estuary; triangle - middle estuary; rectangle - upper estuary; z Pirapama).

Monthly variability of FCO_2 in the estuaries is presented in Figure 5 A and B. In the Capibaribe estuary the values ranged from $106.6 \text{ mmolC m}^{-2} \text{ d}^{-1}$ to $61.62 \text{ mmolC m}^{-2} \text{ d}^{-1}$ between dry and rainy periods, resulting in an annual average of $90 \text{ mmolC m}^{-2} \text{ d}^{-1}$. In the BJ estuary, the average FCO_2 ranged from $117 \text{ mmolC m}^{-2} \text{ d}^{-1}$ to $348 \text{ mmolC m}^{-2} \text{ d}^{-1}$ in the dry and rainy seasons, respectively, resulting in an annual average of $186 \text{ mmolC m}^{-2} \text{ d}^{-1}$. This annual FCO_2 value found for the BJ estuary showed a

considerable influence of the freshwater input, when the maximum values ranged from 180 mmolC m⁻² d⁻¹ in the lower estuary to 653 mmolC m⁻² d⁻¹, in the upper estuary. During the dry season, the average FCO_2 (117 mmolC m⁻² d⁻¹) was close to that found for the Capibaribe (106 mmolC m⁻² d⁻¹).

DISCUSSION

The elevated organic load has driven the nutrient availability in the studied areas especially in the Capibaribe estuary where recurrent phytoplanktonic blooms were registered during the dry period, which was correlated with the elevated concentrations of phosphorus and $DBO_{5,20}$ also influenced by the high residence time of 25 days in the Capibaribe. The rivers flooding increased the TDP, DIN and silicate concentrations and reduce the residence time in the estuaries to values below the previously reported for these estuarine systems in the wet season. Noriega et al. (2013) calculated an average residence time varying from 9-15 days for the Capibaribe estuary and Noriega and Araujo (2011) calculated a residence time of 8-16 days for the BJ estuary. The extreme precipitation event decreased these residence times to ≈ 7 and ≈ 4 days for the Capibaribe and BJ estuaries respectively, thus increasing the transport to the coastal area and such a process brings more organic matter to be mineralized over the continental shelf (Martins et al., 2016).

Different studies discussed about sources of organic matter and dissolved inorganic nutrients to the coast in the Pernambuco state (Noriega and Araujo, 2009; Paulo et al., 2011; Travassos et al., 2016) and trophic state (Flores Montes et al., 2011; Guenther et al., 2015), and they indicated the wastewaters the major source in this interface land-water. Noriega and Araujo (2009) estimated a phosphorus input to the ocean of 37,048 t P y⁻¹, where anthropogenic sources accounted for 99.7% of the emissions.

The link between nutrient dynamics and the ecosystem response under different hydrological regimes on various spatio-temporal scales is still a challenge for the scientific community (Chen and Hong, 2012; Nixon et al., 2015). There are some opposing views, with reports of nutrient enrichment exacerbating the larger scale decline in oceanic pH (Cai et al., 2011; Duarte et al., 2013). While other authors reported that the increase in the primary productivity due to eutrophication may counter the effects of ocean acidification due to the increased productivity leading to CO_2 absorption. (Borges and Gypens, 2010; Guenther et al., 2015).

Despite the increased nutrient concentrations in the river plumes during the wet season, the Chl-*a* and productivity values were higher during the dry season, because of the algal blooms which. Such seasonal variation was also previously reported by Koenig et al. (1995) and Feitosa et al. (1999). Those authors related the decrease in productivity to the increased turbidity in the study area. According to Resurreição et al. (1996), who studied productivity during a seasonal cycle on a transect of the continental shelf in front of the Capibaribe, there is no significant seasonal variation in the chl-*a* concentration at a distance of approximately 4 nautical miles (nm) from the coast.

During the extreme rainfall events of April and May 2011, it was registered the lowest concentrations of CO_3^{2-} with a relative increase in the CO_2 at the same months. Such a variability in the inorganic carbon species must be influenced by the decrease in the primary productivity in the study area during the extreme rainfall months, due the reduced uptake of CO_2 by the phytoplanktonic communities. Several metabolic and diagenetic processes are responsible for the TCO_2 and total alkalinity consumption/production in estuaries. Different authors related that the photosynthesis consumes, and both aerobic and anaerobic organic matter oxidation produce CO_2 . These processes decrease/increase the TCO_2 in seawater, but not the total alkalinity since there is an adjustment of carbonate species and pH according to the equilibrium conditions (Zeebe and Wolf-Gladrow, 2001; Wolf-Gladrow et al., 2007). Sulfate reduction and methane production release HCO_3^- , but also CO_2 and lowers pH, and the final result depends on the total sediment chemistry (Van der Weijden, 1992). Additionally, the anaerobic oxidation of organic matter, which favors HCO_3^- production and increases alkalinity is an important aspect in the alkalinity regulation in polluted estuaries (Frankignoulle et al., 1996; Abril and Frankignoulle, 2001; Abril; Borges, 2004; Thomas et al., 2009).

The input of freshwater with high alkalinity to the Capibaribe and BJ estuaries may counterbalance the free hydrogen ions, except from estuarine organic matter respiration, from natural and anthropogenic sources, which decreases pH. Araujo et al. (2013) calculated the inorganic carbon species for the 2002-2010 period, in a fluvial section of the Capibaribe river, and found values of TCO_2 ranging from 596 to 2235 $\mu\text{mol kg}^{-1}$, increasing over time, and attributed the pattern to an enhanced organic load associated with population growth over the period.

During the study period, it was found a residual organic load of 18.24 t BOD_{5,20} d⁻¹ in the Capibaribe, calculated through the integration of the average annual river's discharge (37.7 m³ s⁻¹) and annual mean BOD_{5,20} (5.6 mg.l⁻¹) ($Q_{\text{mean}} \times \text{BOD}_{5,20\text{mean}}$). The BJ received a residual organic load of 3.25 t BOD_{5,20} d⁻¹. It is 5.6 times less residual organic load than the found in the Capibaribe estuary and may explain the difference in alkalinity found between these estuaries. Since the Capibaribe estuary has a residual volume more elevated than the exchange volume and the BJ estuary has the opposite dynamic, this latter is more susceptible to a CO₂ enrichment and consequently pH decrease, since the organic matter keeps retained inside the estuary where is mineralized.

The prevalence of anaerobic reactions in anoxic estuarine waters and sediments is a drawback to carbonate system calculations using pH and total alkalinity since the real amount of carbonate alkalinity is unknown. The contribution of the organic alkalinity to the TA may be relevant, thus leading to an underestimation of the calculated pCO₂ values using pH and TA (Ko et al., 2016). Such underestimation in the pCO₂ may vary around 30% to 50% (Kuliński et al., 2014). From the low oxygen saturation found in the Barra de Jangadas estuary, <30% throughout the year, and in the Capibaribe estuary during the dry season, as well as the high DBO_{5,20} values and total phosphorus it is possible to assume that the alkalinity from dissolved organic matter probably influence the alkalinity regulation in these estuaries as has recently been discussed by Kullinsky et al. (2014), Abril et al. (2014) and Ko et al., (2016). So further studies are necessary to understand which processes control the alkalinity and the inorganic and organic carbon variability in the Capibaribe and BJ estuaries, including possible submarine groundwater discharge and organic alkalinity contributions.

However, the elevated values found in the present study, with an average pCO₂ in the BJ estuary of 6081 µatm is within the range of 400 to 10000 µatm proposed by Chen et al. (2012) in a review of several studies in estuarine environments. Recently, Noriega et al. (2015) has reported values of pCO₂ in 12 estuaries of northeastern Brazil ranging from 987 to 8970 µatm. Lower pCO₂ values have been reported by Cotovicz et al. (2016) for the Guanabara Bay (418±431 µatm) - an eutrophic ecosystem where the primary productivity significantly lowers the pCO₂ - and in the São Francisco estuary (1469±2948 µatm) which is oligotrophic and dominated by heterotrophy and thus presents higher pCO₂ values.

The rivers' discharge is usually correlated with pCO₂ when there is a significant contribution to the estuary from the upper river (Jiang et al., 2008). The absence of correlation between these parameters in the Capibaribe and BJ estuaries (Figure 8A, B), may be related to the land use in the watershed. The Capibaribe estuary, which is located entirely within an urban area, showed a decrease in pCO₂ during the rainy season, in accordance with previous studies of Noriega et al. (2013). This kind of decrease has also been reported by Abril et al. (2000) in the Scheldt estuary. In such environments, the processes of organic matter mineralization and the microbial respiration rates are the main drivers of CO₂ variability inside the estuary (Zhai et al., 2005; Borges and Guenther et al., 2015).

The variability of CO_{2(aq)} and pH in rivers and estuaries are influenced by the soil CO₂ runoff from wetlands and mangrove areas, which have a potential effect on the process of pCO₂ increase in water bodies, as reported by Abril and Borges (2005), Cai et al. (2011), Sarma et al. (2012) and Abril et al. (2014). The BJ estuary appears to be more susceptible to this type of input because its banks still have dense mangrove areas and extensive wetlands which are exposed during the low tide period. The weak correlation with river discharge ($r^2=0.49$) suggests that it has also been influenced by the high alkalinity freshwater input and the predominance of estuarine biological processes (production/remineralization of organic matter), as compared with advective fluxes. Once estuaries are predominantly heterotrophic ecosystems with high pCO₂ values in the freshwater endmember, decreasing seaward (Chen et al., 2012; 2013) similar to the pattern found in the present study.

The river plumes of the BJ and Capibaribe estuaries, except during the extreme rainy months, acted like autotrophic areas, although their low productivity they were predominantly in a state of CO₂ undersaturation (Figure 5 C, D). During the rainy season in the Capibaribe river plume, especially in May, a CO₂ supersaturation was observed, which has driven the mean flux value of - 4.01 mmolC m⁻² d⁻¹ during the dry season, to a positive mean of + 5.7 mmolC m⁻² d⁻¹ during the rainy season, driven by the influence of the CO₂ rich freshwater.

The average annual CO₂ fluxes found for the urban tropical estuaries evaluated here, of +32,8±20.5 molCm⁻² y⁻¹ and +68.2±58.8 molC m⁻² y⁻¹ for the Capibaribe and BJ estuaries, respectively, are higher than those reported for another tropical Brazilian estuary by Souza et al. (2009) of 13 molCm⁻² y⁻¹ and are above the average for tropical estuaries proposed by Borges et al. (2005) of 17 molC m⁻² y⁻¹.

The FCO_2 average values found in the present study are comparable to those recently reported for 28 estuaries of the northern and northeastern regions of Brazil by Noriega et al. (2014). They proposed a mean value of $20 \pm 16 \text{ molC m}^{-2} \text{ y}^{-1}$ during a normal rainfall season. The FCO_2 averages found in the present study are also comparable to those values proposed by Borges (2005), for polluted environments at mid and high latitudes ($46 \text{ molC m}^{-2} \text{ y}^{-1}$) and the average flux of $62 \text{ molC m}^{-2} \text{ y}^{-1}$ proposed by Frankignoulle et al. (1998) and $68 \text{ molC m}^{-2} \text{ y}^{-1}$ by Chen et al. (2012) for the inner portion of estuaries.

CONCLUSION

The low correlations of pCO_2 with river discharges, which we found in both estuaries, is due to the high alkalinity freshwater input and the predominance of biogeochemical processes of production/remineralization of organic matter, from natural and anthropogenic sources. The high residence time of both estuaries and especially in Barra de Jangadas estuary leads to a CO_2 enrichment of its waters and consequently a pH decrease despite the reduced organic load when compared to the Capibaribe estuary. Such intense organic load is also increasing the nutrients concentrations and lowering the %DO in the study area and also promoting phytoplanktonic blooms during the dry season when the conditions of transparency and high residence time of the waters are favorable to its development. The extreme precipitation event in the Barra de Jangadas estuary led to an increase of nearly 300% in the average pCO_2 values during the months of extreme rainfall. The high TA values found in the freshwater of both estuaries may have a major component of organic alkalinity as seen by the high residual organic loads which these environments are subjected. The final alkalinity balance in these estuaries may constitute an additional buffer to estuarine proton inputs from organic matter respiration. However, further studies are needed to investigate the causes of the alkalinity variability in the area such as submarine groundwater discharges and organic alkalinity contribution. The CO_2 fluxes found for both estuaries are considered high and are comparable to the proposed averages for polluted estuaries in high and intermediate latitudes, illustrating the effects of anthropogenic pressure on rivers and estuaries in densely populated tropical areas.

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