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CENTRO DE TECNOLOGIA E GEOCIÊNCIAS
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THIAGO DE OLIVEIRA CAMINHA

CO_2 SYSTEM PARAMETERS IN ESTUARIES OF PERNAMBUCO

Recife
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Trabalho de Conclusão de Curso apresentado à Coordenação do curso de bacharelado em Oceanografia da Universidade Federal de Pernambuco, como requisito parcial à obtenção do título de Bacharel em Oceanografia.

Orientador: Prof. Dr. Manuel de Jesus Flores Montes.

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ABSTRACT

Carbon dioxide (CO_2) has been intensively emitted to the atmosphere and to the oceans as a consequence of anthropogenic activities, and estuaries are an important understudied ecosystem to set up a global carbon balance due to being a source to the atmosphere. This work assesses spatiotemporal variability of CO_2 system parameters under the influence of tide, salinity and biogeochemical processes in six estuaries of Pernambuco State. Total alkalinity showed a nonconservative behavior in the Santa Cruz Channel, Barra Orange mouth and Capibaribe river estuary, where the latest suffered shifts mainly driven by biogeochemical and anthropogenic related processes suggested by its nutrient richness (nitrogen and phosphorous componds) associated to pollution. All four estuaries (Jaboatão, Ipojuca, Sirinhaém and Formoso rivers) studied in 2019 were oversaturated with respect to CO_2 (except Sirinhaém river – May 17th), where the strongest sources were found in the innermost oligohaline (freshwater during rainy season) Ipojuca river site ($pCO_2 \geq 10770.1$ µatm). The only biological effect on CO_2 of 2019 campaigns was found in the Jaboatão river, between April 8th and May 17th, when a pH decrease from 8.01 to 7.17 was associated with an eutrophic state (Chl-*a* = 30.58 mg m^3). Nevertheless, within each estuary, tidal regime was the main governor of CO_2 system parameters. Despite the expected oversaturation of the studied estuaries, some samples may present miscalculated values of pCO_2 using classic total alkalinity models in its calculations, as contribution of organic compounds to water alkalinity (organic alkalinity) is not considered. Results of this study suggests that human impacts disrupt natural patterns of CO_2 system parameters in estuarine waters. Moreover, further studies with a thorough investigation of buffering capacity of estuarine waters are necessary to better understand CO_2 dynamics, thus leading to more accurate descriptions and new arguments to promote the implementation by local decision makers of mitigation policies on pollution of estuarine waters.

Keywords: CO_2 system. CO_2. Estuary.

RESUMO

Dióxido de carbono (CO_2) vem sendo emitido intensamente para a atmosfera e para os oceanos como consequência de atividades antrópicas, e as águas estuarinas são um componente importante e pouco estudado destas estimativas por ser fonte de CO_2 para a atmosfera. Este trabalho avalia a variabilidade espaço-temporal dos parâmetros do sistema carbonato sob a influência de marés, gradientes de salinidade e processos biogeoquímicos em seis estuários de Pernambuco. A alcalinidade total apresentou comportamento não-conservativo no Canal de Santa Cruz, foz da Barra Orange e estuário do Rio Capibaribe, onde este apresentou variabilidades causadas principalmente por processos biogeoquímicos e atividades humanas, resultados sugeridos pelos altos valores de nutrientes (compostos nitrogenados e fosfatados) associados à poluição. Todos os quatro estuários estudados em 2019 (rios Jaboatão, Ipojuca, Sirinhaém e Formoso) estão supersaturados com relação ao CO_2 (exceto rio Sirinhaém em 17 de maio), dos quais as fontes mais intensas foram encontradas na estação mais interna, no rio Ipojuca, de caráter oligohalino e eventualmente fluvial ($pCO_2 \geq 10770{,}1$ µatm). O único efeito biológico sobre os parâmetros do sistema carbonato dos estuários estudados em 2019 foi observado no rio Jaboatão, entre 8 de abril e 17 de maio, quando uma queda no pH de 8,01 para 7,17 foi associada a um estado eutrófico (Chl-*a* = 30,58 mg m^3). Ainda assim, para cada estuário, o regime de marés foi o principal fator influenciando o sistema carbonato. Apesar da supersaturação de CO_2 esperada para os estuários estudados, algumas amostras podem apresentar valores erroneamente calculados de pCO_2 usando o modelo clássico de alcalinidade total, o qual não considera a contribuição de compostos orgânicos para a alcalinidade da água (alcalinidade orgânica). Os resultados deste trabalho sugerem que os impactos antrópicos geram distúrbios em padrões naturais dos parâmetros do sistema carbonato em águas estuarinas. Ademais, mais estudos que investiguem a capacidade de tamponamento de águas estuarinas são necessários para entender suas dinâmicas do CO_2, os quais levarão a descrições mais precisas e a novos argumentos que promoverão a implementação por tomadores de decisão locais de políticas mitigatórias acerca da poluição de águas estuarinas.

Palavras-chave: Sistema carbonato. CO_2. Estuário.

LIST OF FIGURES

LIST OF TABLES

SUMMARY

1 INTRODUCTION

In a global changes scenario, where carbon dioxide (CO_2) has been intensively emitted to the atmosphere and to the oceans as a consequence of anthropogenic activities (IPCC, 2019; SABINE *et al.*, 2004), the oceans play a major role in the CO_2 cycle (BORGES, 2011; ORR *et al.*, 2005; U. SIEGENTHALER, 1993). They can act as a CO_2 source locally and regionally (ABRIL & BORGES, 2004; FLECHA *et al.*, 2015; FRANKIGNOULLE *et al.*, 1996a), but globally the oceans are reported to behave as a CO_2 sink (DONEY *et al.*, 2009; HÖNISCH *et al.*, 2012; ORR *et al.*, 2005; SABINE *et al.*, 2004). Higher seawater concentrations of CO_2 may induce a drop in its pH, a process known as ocean acidification, which could cause great impacts to oceans chemistry (FEELY *et al.*, 2009; MILLERO, 2007a), physics (HESTER *et al.*, 2008) and biology (ALBRIGHT *et al.*, 2016; HOEGH-GULDBERG *et al.*, 2007; ROSSI *et al.*, 2018), as well as for world's economy and public health (BRANDER *et al.*, 2012; COOLEY & DONEY, 2009; SANDIFER & SUTTON-GRIER, 2014).

CO_2 dynamics in aquatic environments needs to be better understood, especially in coastal and estuarine waters due to its biogeochemical complexity (BORGES, 2011). In such waters, as for the oceans, three main processes govern its CO_2 content, known as the physical, biological and chemical pumps (Eq. 1-3). Borges & Abril (2012) reported that 61 out of 62 studied estuaries around the world behave as a source of CO_2 to the atmosphere in several studies, pointing the net heterotrophy (respiration > primary production) and the inputs of rivers of CO_2 rich freshwaters as the major reasons for the observed trend. Moreover, these waters commonly experience unnatural shifts by local and regional human intervention because of its proximity to urban areas, further with the global changes seen nowadays. For instance, the physical pump (Eq. 1) is directly affected by global warming, thermal pollution, soil impermeabilization and salinization of watersheds (i.e. alteration of water density and thus gas solubility - (WEISS, 1974)), along with direct input of CO_2 by air-sea exchange due to higher emissions from burning fossil fuels (SABINE *et al.*, 2004). Also, eutrophication and direct organic matter (OM) input caused by domestic waste can disturb the biological pump (Eq. 2), as CO_2 is produced with a decrease of local net metabolism (= primary production - respiration) and increase of OM aerobic degradation by bacteria (BORGESA & GYPENSB, 2010; COTOVICZ *et al.*, 2015). Lastly, the chemical pump (i.e. the CO_2 system - Eq. 3) tends to be unbalanced by changes in total alkalinity (A_T) and pH due to inadequate use of soils (CAI & WANG, 1998a; WANG & CAI, 2004), mineral exploitation and industrial waste (changes in bicarbonate and carbonate input), which in turn can act synergistically with unexpected physical and biological changes to disturb CO_2 dynamics and it's natural functioning.

$$CO_{2(atm)} \leftrightarrows CO_{2(aq)} \tag{1}$$

$$6CO_{2(aq)} + 6H_2O \leftrightarrows C_6H_{12}O_6 + 6O_2 \tag{2}$$

$$CO_{2(aq)} + H_2O \leftrightarrows H_2CO_3 \leftrightarrows H^+ + HCO_3^- \leftrightarrows 2H^+ + CO_3^{2-} \tag{3}$$

As verified by several authors, coastal and estuarine waters could contribute significantly to CO_2 budgets estimations, as these waters commonly behave as a source of CO_2 to the atmosphere (ARAUJO *et al.*, 2013; BORGES & ABRIL, 2012b; CHEN *et al.*, 2013; NORIEGA & ARAUJO, 2014). Chen *et al.* (2012) reported a global estuarine flux of 0.26 Pg C yr^{-1}. Later, Chen *et al.* (2013) reported that 165 estuaries around the world export 0.094 Pg C yr^{-1}. Those figures, if taken into account, could lead to a more accurate global carbon estimation than that reported by Sabine et al. (2004) of 0.61 ± 0.09 Pg C yr^{-1}. As discussed in the abovementioned studies, such estimations are made possible by investigating CO_2 system parameters, where partial pressure of CO_2 (pCO_2) gives information about CO_2 fluxes between the air-sea interface.

pCO_2 values can be inferred by two methods: measuring it directly or calculating it using a seawater model (DOE, 1994; MILLERO, 2007), where thermodynamic relations between total alkalinity (A_T), pH, dissolved inorganic carbon (C_T) and pCO_2 (CO_2 system parameters) allow calculation of two of these parameters when the other two are known. Calculated pCO_2 data are more commonly found than measured pCO_2 around the world, where this parameter is commonly based on measurements of pH/A_T and seawater temperature in most cases (ABRIL *et al.*, 2015a). However, ABRIL *et al.* (2015b) also noticed that some publications report extremely high and potentially biased pCO_2 values in systems with low alkalinity and pH and high dissolved organic carbon (DOC) such as estuaries, where calculated pCO_2 was >100% higher (median overestimation of 9080 ppmv) than measured pCO_2 in the 25% most organic-rich and acidic samples. Several studies described that the influence of organic alkalinity (A_{org}) is behind these errors, which are often neglected in chemical models of seawater (KIM *et al.*, 2006). First, (BRADSHAW & BREWER 1988) inferred organic acids and bases presence in seawater by noting a discrepancy between the total inorganic carbon estimated from titration data and that from an extraction procedure. Then some studies showed that this influence may be caused by organic compounds from numerous sources, such as humic materials (CAI *et al.*, 1998b; ULFSBO *et al.*, 2015), negatively charged surface groups on phytoplankton and bacterial cells (KIM *et al.*, 2006) and phytoplankton production of dissolved organic matter (DOM) during photosynthesis (KIM & LEE, 2009; KO *et al.*, 2016).

By analyzing CO_2 system parameters and other oceanographic variables such as tides, temperature, salinity and nutrients in different estuaries of Pernambuco under different weather conditions, the main goal of the present work is to assess the spatiotemporal distribution of the CO_2 system parameters in estuarine waters of Pernambuco State, as well for biogeochemical processes involved in their variabilities.

2 METHODS

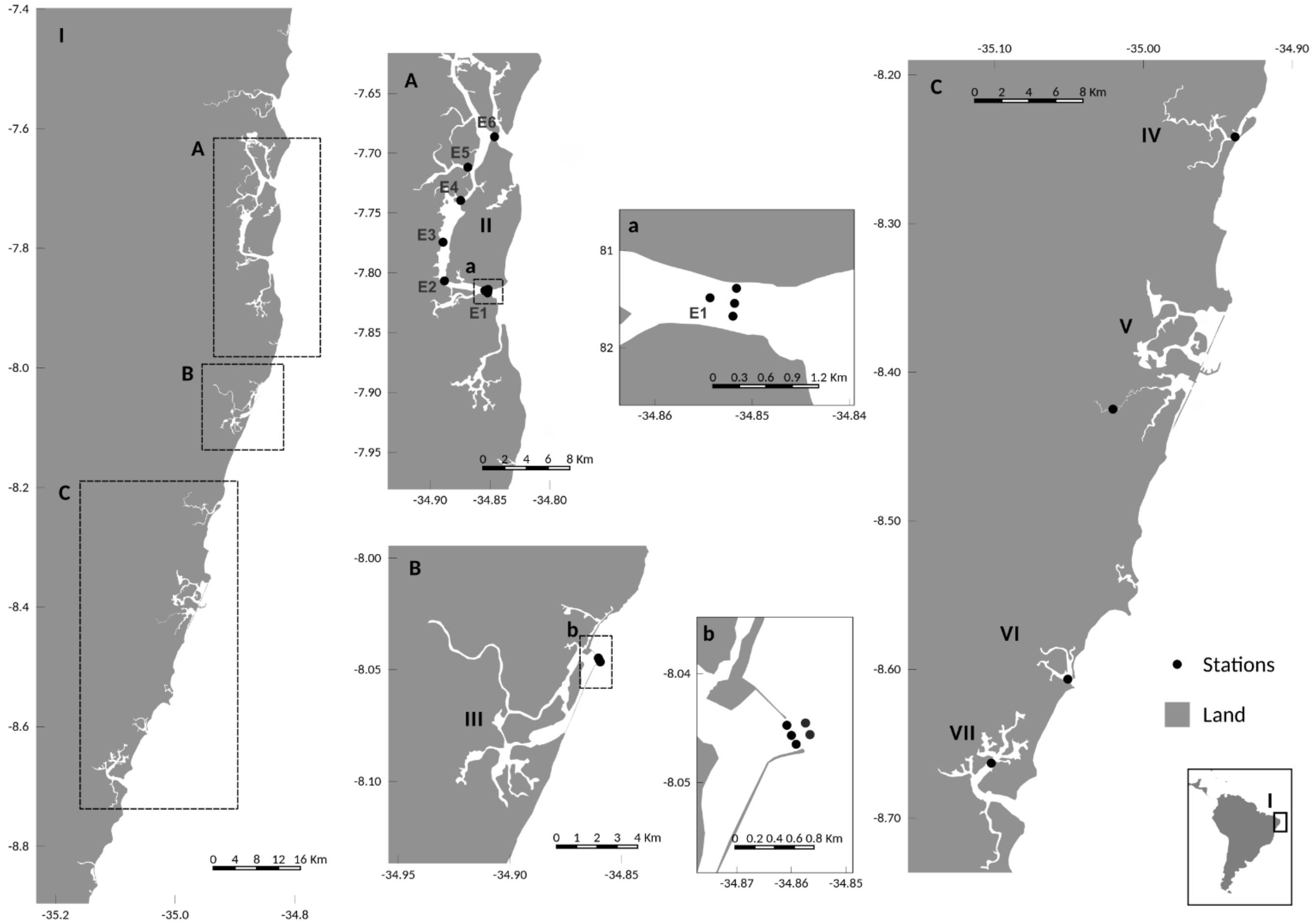
In this section, the study area is briefly described with a focus on oceanographic features and human use in order to provide the essential information around the studied issue. Then, sampling strategy, analysis and calculations that were performed during the elaboration of this work are described.

2.1 STUDY AREA

The coastline of Pernambuco is approximately 187 km long, representing 2.5 % of the total length of Brazil's coastline (7,379 km) and contains twenty-one coastal cities (MMA, 2018). Two distinct seasonal periods are typical in this area, dry and wet seasons, which often take place on October, November and December and May, June and July, respectively, while remaining months are usually transition periods regarding rainfall. Pernambuco's continental shelf is influenced by the South Equatorial Current, warm and CO_2 rich waters formed at east Atlantic (LEFÉVRE *et al.*, 2010). Despite the oligotrophic feature of its coastal waters, Pernambuco's coast is known for having several locally important marine ecosystems in terms of ecology and economics (e.g. estuaries and coral reefs). Its shelf hosts an abundant community of calcifying organisms such as coralline algae banks of the genus *Halimeda* (BANDEIRA-PEDROSA *et al.*, 2004) and extensive coral reef lines (LEÃO *et al.*, 2016) that could be directly endangered by acidification processes (ALBRIGHT *et al.*, 2016; GATTUSO *et al.*, 1998; LANGDON *et al.*, 2000).

Within the 29 watersheds residing in the state of Pernambuco, 6 mesotidal estuaries and estuarine complexes were studied in the present work: estuarine complex of Santa Cruz channel (SCC) and its southern bar, Barra Orange (BO), Capibaribe river lower estuary (CE), Jaboatão river estuary (JE), upper estuary of Ipojuca River (IPE), Sirinhaém (SE) and Formoso rivers (FE) (Figure 1). In spite of their small size, together the 6 studied estuaries are their basins' main drainage route for an area of approximately 57631 km^2 (CPRH, 2017).

Figure 1 – Study area with sampling sites along the coast of Pernambuco (**I**).



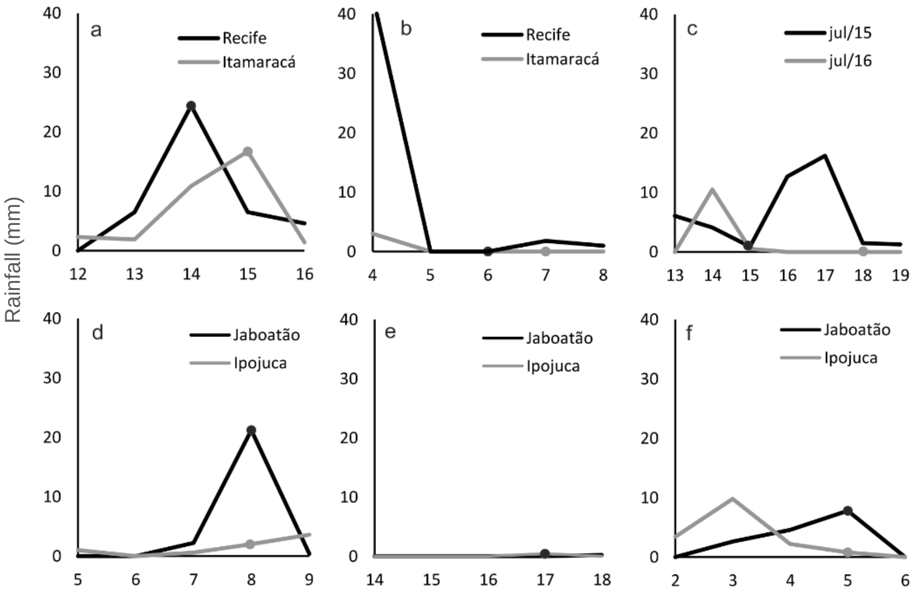
Source: CPRH, 2017. Figure of own authorship.

Studied estuaries are represented as follows: Santa Cruz Channel (**II**), Barra Orange (**II - a**), Capibaribe river lower estuary (**III – b**), Jaboatão river lower estuary (**IV**), upper estuary of Ipojuca river (**V**), Sirinhaém (**VI**) and Formoso (**VII**) river lower estuaries. Sampling sites are represented by black dots.

They provide countless socioecological and economical services and have been used for urban and industrial occupation, agriculture, public supply, domestic and industrial effluents, as well as for tourism, fisheries and transportation (CPRH, 2017). Therefore, it is essential to maintain investigation on biogeochemistry about these environments, as they represent great importance for the society and are under constant human pressure.

In order to assess precipitation influence over the studied environments, data of daily precipitation around sampling dates were taken from Agência Pernambucana de Águas e clima (APAC) (Figure 2), once the rivers in question show relatively low discharges (CPRH, 2017).

Figure 2 – Daily precipitation around sampling dates.



Source*:* APAC, 2019. Figure of own authorship.

Sampling design 1 (**a** – May 14th and 15th of 2014, **b** – November 6th and 7th of 2014), **sampling design 2** (**c** – July 15th of 2015 and July 18th of 2016) and **sampling design 3** (**d** –April 8th, **e** – May 17th, **f** – July 5th, those from 2019). Black and grey dots represent actual rainfall at sampling dates.

2.2 SAMPLING

Three distinct sampling designs were performed along 6 estuaries (Figure 1) in order to assess spatiotemporal variability of pH and total alkalinity, two carbon dioxide parameters, under the influence of other oceanographic factors such as tides, salinity gradients and inorganic nutrient concentration.

2.2.1 Barra Orange and Capibaribe river lower estuary – sampling design 1

Four diurnal sampling campaigns were performed, two (May 14th and November 06th) in the more impacted estuary, CE, and two (May 15th and November 07th) in the less impacted estuary, BO, to compare the studied parameters in surface water samples of both areas under different seasonal periods. Total alkalinity (A_T) data was the focus of this sampling campaign as it is an important component of the CO_2 system, while its possible main drivers were investigated by the analysis of the variables temperature (T), salinity (S), suspended particulate matter (SPM), dissolved oxygen (DO), nitrite (NO_2^-), nitrate (NO_3^-), total nitrogen (N_T), ammoniacal nitrogen (NH_3/NH_4^+), total dissolved silicate ($Si(OH)_4$) and total dissolved inorganic phosphorous (PO_4^{3-}). For each sampling campaign, a transect with five (CE) and three (BO) stations were determined transversally to the mouth and equidistantly to each other, and samples were taken within an interval of 3 hours during a tidal day cycle to assess diurnal variability of the studied parameters (Figure 1 – a, b).

2.2.2 Santa Cruz Channel – sampling design 2

Two sampling campaigns were performed in July 15th and 18th of 2015 and 2016, respectively, to evaluate spatial and temporal variability of the studied parameters in surface water samples of six stations along the SCC. Total alkalinity (A_T) data was the focus of this sampling campaign as well, while its possible main drivers were investigated by the analysis of the variables temperature, salinity, suspended particulate matter, dissolved oxygen, nitrite, nitrate, total nitrogen, ammoniacal nitrogen, total dissolved silicate, total dissolved inorganic phosphorous and chlorophyll *a* (Chl-*a*). Samples were collected from the station one (E1) to station six (E6) during the low tide, and from E6 to E1 during high tide, in order to assess salinity gradients and influence of tidal stages upon the studied parameters (Figure 1 – A).

2.2.3 Estuaries of south coast of Pernambuco - sampling design 3

Three sampling campaigns were taken in April 08th, May 17th and July 05th of 2019. For each sampling date, a single surface water sample was collected in a single station at the lower estuaries of the JE, SE and FE and the upper estuary of IPE, in order to compare carbon dioxide parameters between each estuary under different precipitations. Total alkalinity and pH were analyzed, and pCO_2, dissolved inorganic carbon (C_T), carbon dioxide (CO_2), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}) and calcite saturation (ΩCa) were calculated using CO2SYS®. Possible drivers of CO_2 system variabilities were investigated using data of temperature, salinity, suspended particulate matter, dissolved oxygen, nitrite, nitrate, ammoniacal nitrogen, total dissolved silicate, total dissolved inorganic phosphorous and chlorophyll *a*.

2.3 ANALYSIS

Temperature (T) and salinity (S) data were taken in situ with CTD equipment. Dissolved oxygen (DO), nitrite (NO_2^-) and nitrate (NO_3^-) analysis followed methods described by STRICKLAND & PARSONS (1972), while total nitrogen (N_T), ammoniacal nitrogen (NH_3/NH_4^+), total dissolved silicate ($Si(OH)_4$) and total dissolved inorganic phosphorous (PO_4^{3-}) were analyzed as described by GRASSHOFF *et al.* (1999). Samples for A_T-pH were poisoned with $HgCl_2$ and taken to the *Laboratório de Oceanografia Química (LOQUIM)* for further analysis, where A_T was measured by automatic potentiometric titration with an open cell and pH, using total scale, by spectrophotometry with m-cresol purple indicator, both following well described methods by DOE (1994). All calibration and validation of A_T-pH analysis were made using certified reference materials (CRM) provided by Andrew Dickson (Scripps Institution of Oceanography, San Diego, USA). A_T analysis had a precision of 15 μmol kg^{-1} and an accuracy of 98% for sampling designs 1 and 2, while sampling design 3 had a precision of 1 ± 6 μmol kg^{-1} and an accuracy of 99.4% for A_T analysis and a precision of 0.00805 ± 0.00855 and an accuracy of 99% for pH analysis.

2.4 CALCULATIONS

All calculations regarding CO_2 parameters were made using the CO2SYS® software (ver. 2.1, Atlantic Oceanographic and Meteorological Laboratory (AOML), National Oceanic and Atmospheric Administration (NOAA), see https://cdiac.ess-dive.lbl.gov/ftp/co2sys/) with the dissociation constants for H_2CO_3 provided by DICKSON & MILLERO (1987) along with S, T, $Si(OH)_4$ and PO_4^{3-} data for maximum precision. For low salinity waters calculations used constants of MILLERO *et al.* (2006). pCO_2, dissolved inorganic carbon (C_T), carbon dioxide (CO_2^*), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}) and ΩCa were calculated using the measured pair A_T-pH.

In order to assess miscalculations regarding inorganic CO_2 system parameters due to a possible significant A_{org} contribution to A_T, the difference between A_T (measured) and inorganic alkalinity (A_{inorg}) was calculated as follows.

$$\Delta A = A_T - A_{inorg} \tag{4}$$

$$A_{inorg} = A_{carb} + A_B + A_{OH} + A_P + A_{Si} \tag{5}$$

$$A_{carb} = [HCO_3^-] + 2*[CO_3^{2-}] \qquad (6)$$

Boron, hidroxyl, phosphoric and siliceous alkalinities (A_B, A_{OH}, A_P and A_{Si} respectively) were also calculated using the CO2SYS® software. Statistical analysis were performed using software JMP® version 10.0.0 by SAS institute, where Mann-Whitney test ($\alpha = 0.05$) was performed to investigate seasonal trends and Principal Components Analysis (PCA) to evaluate correlations between measured variables.

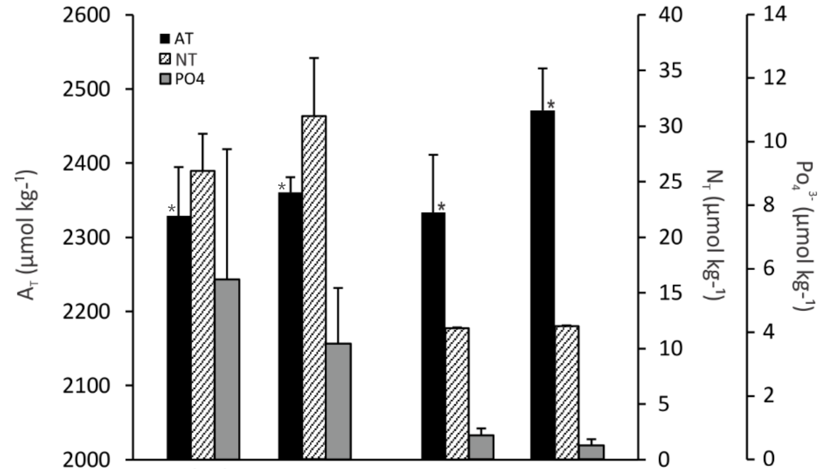
3 RESULTS AND DISCUSSION

Each of the three performed sampling designs are individually discussed by the following subsections, in order to allow discussion of further details. Then, general concluding remarks are summarized in the last section.

3.1 BARRA ORANGE AND CAPIBARIBE RIVER LOWER ESTUARY

A_T was substantially different (Mann-Whitney test, $p<0.0001$) between seasons in the less impacted estuary, with lower nutrient concentrations, the BO (Figure 3, Table 1), even though rainfall variations (Figure 2) were not sufficient for significantly changing S for the BO (Mann-Whitney test, $p = 0.88$). A similar trend was found in previous studies in pristine estuaries (HOWLAND *et al.*, 2000; WANG & CAI, 2004) and other estuaries considered polluted (ABRIL *et al.*, 2003; ABRIL & FRANKIGNOULLE, 2001; GASPAR *et al.*, 2018; MANAKA *et al.*, 2015; NORIEGA *et al.*, 2015).

Figure 3 - Seasonal variations of means of A_T, N_T and PO_4^{3-}.



Source*: own authorship.*

Legend - Significant differences between seasons within an estuarine system are marked with asterisk.

However, despite the significant difference observed for A_T means between seasons in CE according to Mann-Whitney test (Mann-Whitney test, $p = 0.0230$), high variance of wet season A_T values and very low difference between seasonal means in comparison with the BO (Table 1) suggest that dilution effect on A_T - caused by the increased freshwater input from precipitation – could be being counterbalanced by pollution (Figure 3). The Government Environmental Agency reported that the Capibaribe River basin is strongly impacted by agricultural and domestic wastewater, which is rich in organic matter and inorganic nutrients from a high population density urban area (CPRH, 2017). For the wet season, higher content of PO_4^{3-} associated with lower DO concentrations indicates a possible eutrophication process, leading to an OM buildup and favoring it's anaerobic degradation, which is described as an addition process for the A_T by adding HCO_3^- to the system (CAI & WANG, 1998a). Additionally, human intervention on the course of the Capibaribe river and its drainage basin could represent another source of A_T, once concrete weathering inputs HCO_3^- and is intensified during increased river flow (RAYMOND & HAMILTON, 2018). However, it is important to consider the geological features of the Capibaribe river basin as an important natural contributor to A_T in view of the marked presence of carbonate and chalky-silicate rocks, which also inputs HCO_3^- due to chemical weathering (NEVES *et al.* 2013).

Table 2 - Mean, minimum and maximum of studied parameters by season and study area.

	CE		BO	
	May 14th	**Nov 6th**	**May 15th**	**Nov 07th**
n	16	16	13	10
T (C°)	28.46 (27.6 – 29.08)	-	28.88 (28.46 – 29.41)	28.42 (27.51 – 29.18)
S (psu)	29.62 (22 – 35.49)	-	34.62 (31.96 – 35.97)	34.82 (35.05 – 36.4)
MPS (mg L^{-1})	37.23* (21.8 – 52.2)	31.30* (3.8 – 155.4)	35.82 (25.8 – 48.2)	-
NO_2^- (µmol kg^{-1})	0.32* (21.8 – 0.6)	0.81* (3.8 – 0.1)	0.24* (0.06 – 0.68)	0.02* (0 – 1.13)
NO_3^- (µmol kg^{-1})	2.60* (0.17 – 7.21)	4.63* (2.99 – 8.6)	1.25* (0.47 – 2.21)	0.65* (0.09 – 1.41)
NH_3/NH_4^+ (µmol kg^{-1})	4.11 (0.05 -09.65)	7.23 (0.2 – 16.95)	0.06* (0 – 0.23)	0.01* (0 – 0.11)
N_T (µmol kg^{-1})	25.95 (9.84 – 41.14)	30.84 (3.76 – 54.8)	11.82 (5.96 – 17.79)	12 (6.99 – 22.22)
PO_4^{3-} (µmol kg^{-1})	5.68 (0.87 – 13.31)	3.65 (0.34 – 6.5)	0.76* (0.38 – 1.16)	0.43* (0.05 – 0.7)
$Si(OH)_4$ (µmol kg^{-1})	39.46 (6.95 – 88.95)	21.08 (7.67 – 45.28)	8.87 (3.37 – 19.91)	6.53 (2.8 - 12)
DO (mL L^{-1})	2.19 (0.25 – 4.3)	3.10 (1.25 – 5.05)	4.23 (2.98 – 5.84)	4.25 (3.12 – 5.16)
A_T (µmol kg^{-1})	2329.07* (2231 – 2456)	2360.50* (22320.45 – 2395.3)	2333.38* (2233 - 2475)	2471.39* (2377.25 – 2534.75)

Source*:* own authorship

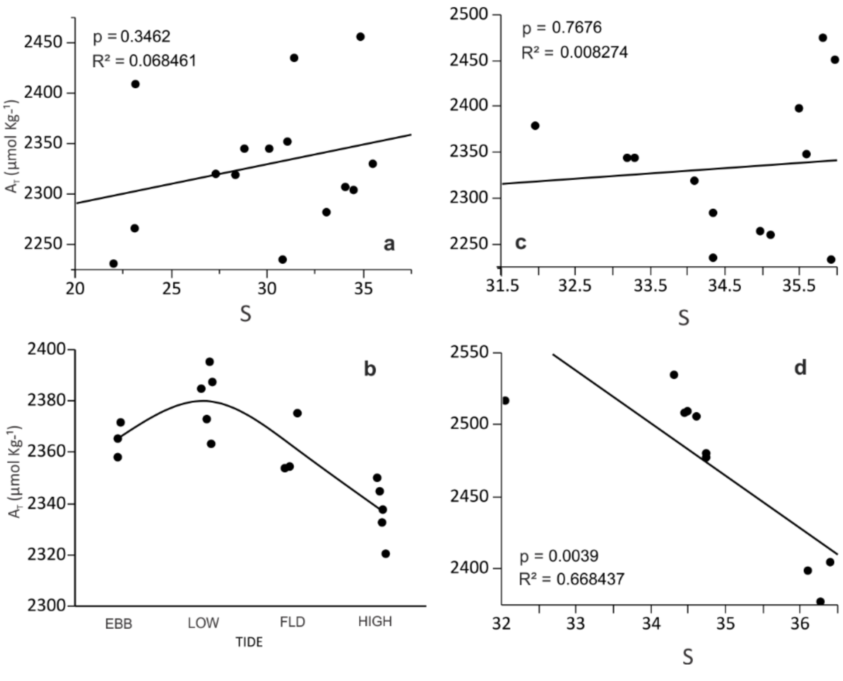
Legend - Seasonal differences within each study area were investigated with Mann-Whitney test, where significant differences were marked with an asterisk.

On the other hand, superior concentrations of N_T and nitrate was detected for the dry period, indicating that the nitrification process could be behind the A_T

consumption, once two free protons are released to the water for each nitrate produced, and thus consume two equivalents of alkalinity (ABRIL & FRANKIGNOULLE, 2001; FRANKIGNOULLE *et. al.*, 1996b). Together, different prevailing biogeochemical processes shifted $A_{T,}$ affecting its natural seasonal variability. In addition, one could reason that, indeed, nitrogen compounds are good organic matter indicators, and OM degradation is a source of CO_2 that could be consuming A_T. However, all the concentrations of A_T expression change according to the pH decrease from H_2CO_3 production and thus remain constant despite the CO_2 input (WOLF-GLADROW *et al.*, 2007).

The investigation of tidal influence showed that A_T data from CE and BO revealed a nonconservative behavior, in agreement with previous studies (ABRIL *et al.*, 2003; CAI & WANG, 1998a; KEMPE, 1990), once the dilution effect was not the only factor involved in A_T variations (Figure 4). BO exhibited a negative trend with S at the dry season, presenting the only good linear regression for all campaigns ($R^2 = 0.67$, $p = 0.0039$, dry period), although some high S (>35.5) samples from the rainy season suffered a great addition (Figure 4 – c).

Figure 4 - Tidal influence over A_T values in CE and BO.

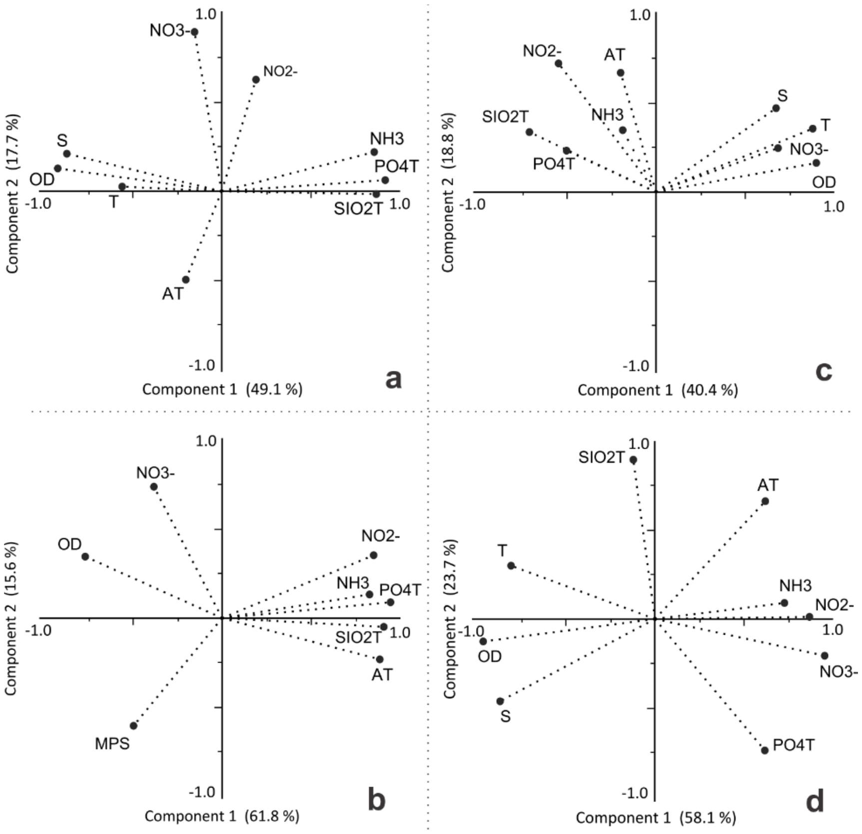


Source: own authorship.

Legend - CE (**a** – March 2014, **b** – November 2014), BO (**c** – March 2014, **d** – November 2014). Solid black lines represent regression lines in **a**, **c** and **d**, while tendency line in **b**.

PCA results expressed that principal component 1 (PC1) explained most of the data variation and represented tidal influence as the main process of the studied parameters for CE during wet season, and for BO during dry and wet seasons (Figure 5 – ac and d). However A_T did not show good correlations with any other variables, not even with S (PCA_{corr} = 0.01), corroborating with the assumption that A_T has an additional allochthonous input, probably associated with human activities. Such environmental complexity due to anthropogenic intervention was also observed at CE in the same period, once parameters made little effect on A_T.

Figure 5 - PCA assembling all studied parameters within each local and period for CE and BO.



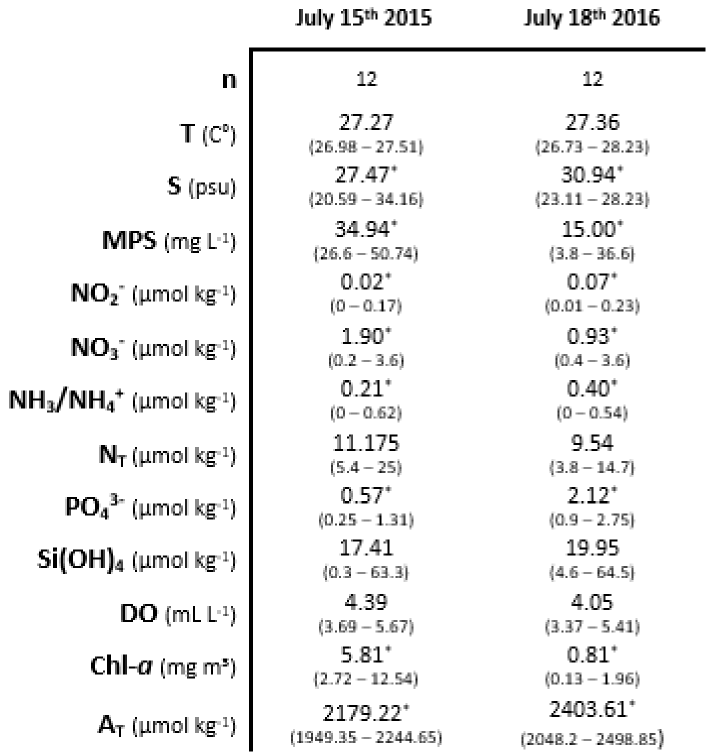
Source: own authorship.

Legend - CE (**a** – March 2014, **b** – November 2014), BO (**c** – March 2014, **d** – November 2014).

3.2 SANTA CRUZ CHANNEL

Results for SCC showed that, except for T, N_T, $Si(OH)_4$ and DO, all parameters were significantly different between seasons (Table 2). A_T had lower mean for the wet period (2179.22 ± 84.64 µmol kg^{-1} - wet period; 2403.61 ± 120.38 µmol kg^{-1} – dry period), a trend that demonstrates a less impacted environment, once A_T variability is highly influenced by changes in alkaline compound concentrations due to higher freshwater inputs from rainfall, according to the definition described by Millero (2007).

Table 2 - Mean, minimum and maximum of studied parameters of the SCC by season.



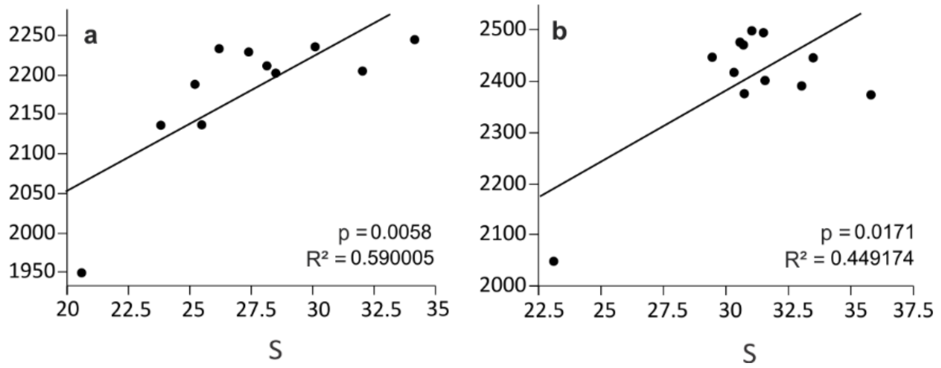
	July 15th 2015	July 18th 2016
n	12	12
T (C°)	27.27 (26.98 – 27.51)	27.36 (26.73 – 28.23)
S (psu)	27.47^{*} (20.59 – 34.16)	30.94^{*} (23.11 – 28.23)
MPS (mg L^{-1})	34.94^{*} (26.6 – 50.74)	15.00^{*} (3.8 – 36.6)
NO_2^- (µmol kg^{-1})	0.02^{*} (0 – 0.17)	0.07^{*} (0.01 – 0.23)
NO_3^- (µmol kg^{-1})	1.90^{*} (0.2 – 3.6)	0.93^{*} (0.4 – 3.6)
NH_3/NH_4^+ (µmol kg^{-1})	0.21^{*} (0 – 0.62)	0.40^{*} (0 – 0.54)
N_T (µmol kg^{-1})	11.175 (5.4 – 25)	9.54 (3.8 – 14.7)
PO_4^{3-} (µmol kg^{-1})	0.57^{*} (0.25 – 1.31)	2.12^{*} (0.9 – 2.75)
$Si(OH)_4$ (µmol kg^{-1})	17.41 (0.3 – 63.3)	19.95 (4.6 – 64.5)
DO (mL L^{-1})	4.39 (3.69 – 5.67)	4.05 (3.37 – 5.41)
Chl-*a* (mg m^3)	5.81^{*} (2.72 – 12.54)	0.81^{*} (0.13 – 1.96)
A_T (µmol kg^{-1})	2179.22^{*} (1949.35 – 2244.65)	2403.61^{*} (2048.2 – 2498.85)

Source: own authorship.

Legend - Seasonal differences were investigated with Mann-Whitney test, where significant differences were marked with an asterisk grouped by Student's T test.

The investigation of A_T under a salinity gradient revealed a nonconservative behavior, in agreement with results found for the previously described CE and BO. A positive trend with salinity was observed by the performed regressions for both wet ($R^2 = 0.59$, $p = 0.0058$) and dry periods ($R^2 = 0.45$, $p = 0.0171$), in accordance with Noriega & Araujo (2014) and Gaspar *et al.* (2018) for other estuaries of Pernambuco, even though highest values were noticed for intermediate values of S (Figure 6).

Figure 6 - A_T data under salinity gradients at SCC.



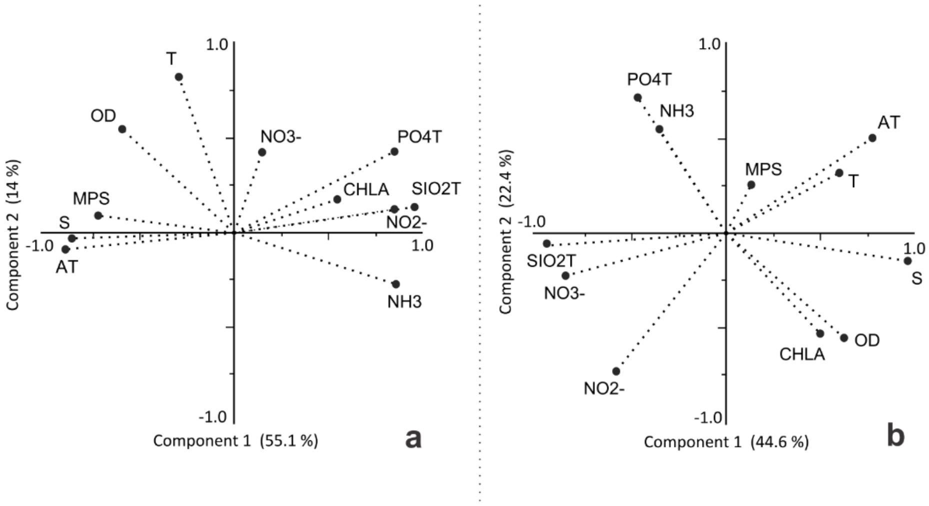
Source: own authorship.

Legend - wet (**a**) and dry (**b**) seasons are described, in which regression is represented by solid black lines.

According to Medeiros & Kjerfve (1993), the SCC experiences a weakening of its water exchange with the coastal zone along with its dissolved and suspended materials. That process occurs because of a salinization due to higher evaporation rates overcoming precipitation observed for that area. Thus, by increasing inner waters residence time, this process could explain the retention of A_T in the middle reaches of the SCC. Also, the high evaporation rate itself could be enhancing alkalinity of its waters by water loss, a mechanism described by Cai et al. (2008) at the Mississippi and Huang he rivers. Furthermore, greater freshwater influence by the Botafogo river on station 5 of SCC had the lowest values of A_T of 1949.35 µmol kg^{-1} and 2048.2 µmol kg^{-1} for the wet and dry months, respectively, showing that such estuarine complex is also highly influenced by river discharge (MEDEIROS & KJERFVE, 1993).

PCA analysis showed that PC1 represented the dilution effect as the main driver of data variability. In general, S had a good positive correlation with AT and DO and a negative correlation with nutrients for both sampling campaigns (Figure 7). As reported by Pereira (2017) with the same dataset, the trophic state index (TRIX) (a method described by Vollenweider *et al.* (1998)) of SCC ranged between 2.58 and 4.10, indicating predominantly good quality waters. PCA and TRIX information together show that, despite of an increase of human activities which the study site is facing since 2007 (PEREIRA, 2017), the system has been resilient with respect to water quality by the years of 2015 and 2016, and therefore, AT showed an expected pattern mainly regulated by natural processes, such as dilution effect and nitrification.

Figure 7 - PCA assembling all studied parameters of wet (**a**) and dry (**b**) seasons from SCC.

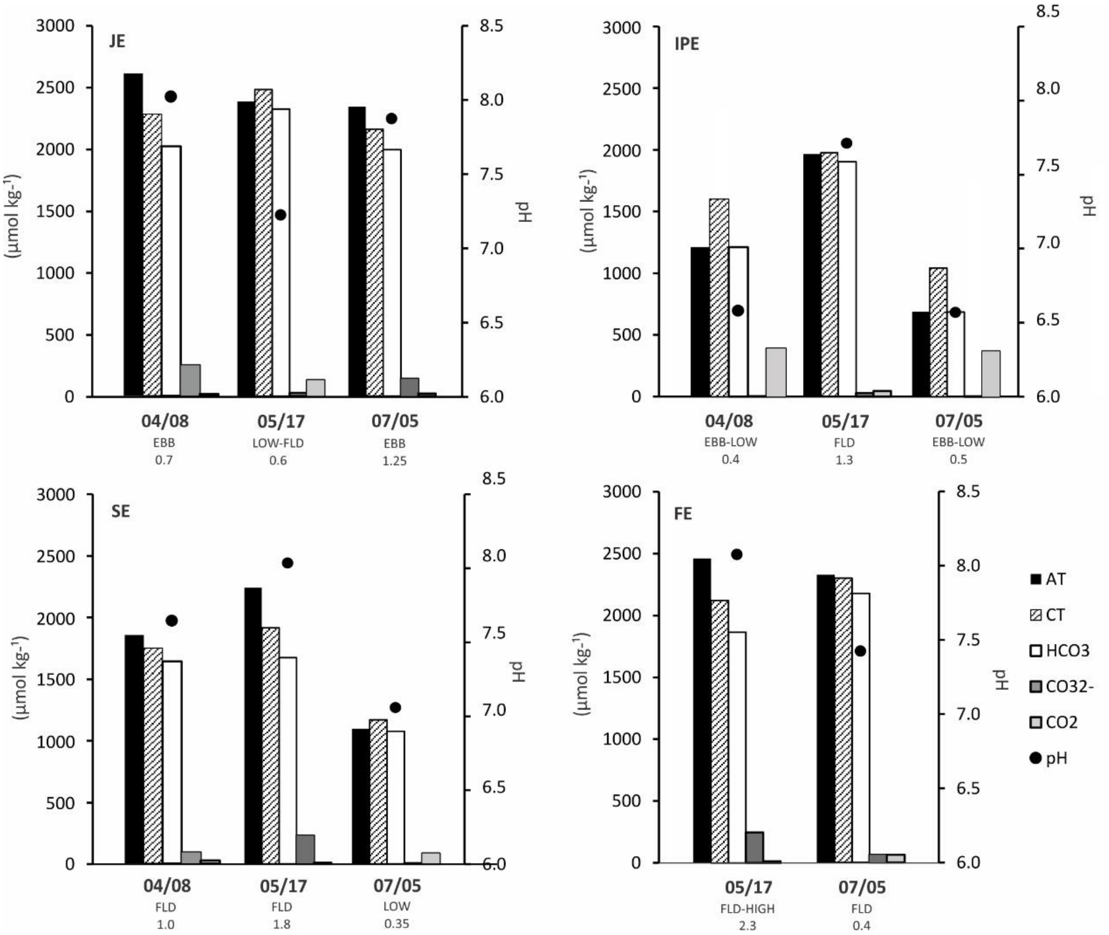


Source: own authorship.

3.3 ESTUARIES OF SOUTH COAST OF PERNAMBUCO

Decoupling of seasonality and tidal regime effects was difficult for the sampling of 2019, and apparently the latter was the main driver shifting CO_2 system parameters (Figure 8). In fact, the only detectable rainfall influence was observed at IPE, where a notable drop of S (2.8 to 0.2, Table 3) and carbonate content (A_T – 1259.77 µmol kg^{-1} to 689.1 µmol kg^{-1}, C_T – 1662.8 µmol kg^{-1} to 1043 µmol kg^{-1}) occurred between April 8th and July 5th for the same tidal height (Ebb-Low tides, 0.4 m and 0.5 m respectively), suggesting that salinity imposed a stronger influence over those parameters in comparison to continental runoff.

Figure 8 - Total alkalinity (A_T), dissolved inorganic carbon (C_T), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), carbon dioxide (CO_2) and pH data for each sampling campaign of estuarine systems studied in 2019 (JE, IPE, SE and FE).



Source: own authorship.

Tidal regime (EBB: ebb tide; LOW: low tide; FLD: flood tide; HIGH: high tide; LOW-FLD: beginning of the flood tide; EBB-LOW: ending of the ebb tide; FLD-HIGH: ending of the flood tide) and tidal height (in meters) are described under each sampling date label.

Despite the above mentioned oligohaline character of the IPE station, which is expected to show high productivity rates associated with low buffering capacity and thus an acidic and CO_2 rich water (ABRIL *et al.*, 2015; BORGES & ABRIL, 2012; CHEN *et al.*, 2012), it presented low CO_2 content in a sampling campaign (May 17th) in comparison with the others. Pushing of the material retention region riverward by the flooding tide increased C_T and A_T and buffering capacity of the system, neutralizing free H^+ from H_2CO_3 (CO_2 from 404.5 μmol kg^{-1} to 44.7 μmol kg^{-1}) and increasing its pH (from 6.60 to 7.71) and decreasing pCO_2 (from 13534.1 μatm to 1569.8 μatm) between April 8th and May 17th (Table 3, Figure 8). As for the SE, the lowest tide sampling (July 5th) was mesohaline (S = 12.93) and had the lowest buffering capacity for this site (A_T = 1094.47 μmol kg^{-1}), leading to a pH decrease by almost 1.0 (8.03 to 7.06) and a CO_2

oversaturation (pCO_2 = 2899.2 µatm). FE also exhibited an acidifying trend attributed to estuarine influence and buffering capacity decrease.

Table 3 - Data from 2019 sampling campaigns. *Source: own authorship.*

	JE			IPE			SE			FE	
	04/08	05/17	07/05	04/08	05/17	07/05	04/08	05/17	07/05	05/17	07/05
T (C°)	30.40	29.40	27.80	29.40	31.30	26.10	30.30	30.40	27.42	30.30	28.80
S (psu)	30.70	16.80	32.20	2.81	3.40	0.20	26.80	34.30	12.93	35.30	33.85
MPS (mg L^{-1})	17.40	8.33	-	8.60	10.89	-	14.00	11.20	-	7.40	-
NO_2^- (µmol kg^{-1})	0.30	1.08	0.27	0.08	1.13	0.47	0.20	0.02	0.13	0.02	0.06
NO_3^- (µmol kg^{-1})	1.36	8.20	3.30	4.04	8.70	29.70	3.94	1.40	4.10	1.00	ND
NH_3/NH_4^+ (µmol kg^{-1})	3.38	3.66	1.98	1.95	3.69	0.18	1.27	1.35	0.72	0.85	0.16
P_T (µmol kg^{-1})	4.37	0.91	1.27	0.43	1.02	3.18	0.50	0.28	0.13	0.11	0.22
$Si(OH)_4$ (µmol kg^{-1})	67.50	81.10	15.70	20.00	110.30	146.90	60.50	19.10	151.60	8.60	35.50
DO (mL L^{-1})	3.51	1.77	3.80	1.59	2.71	3.82	4.83	4.64	3.93	4.68	3.99
Chl-*a* (mg m^3)	7.59	30.58	8.20	11.67	2.64	1.33	3.05	4.71	1.64	3.60	3.57
A_T (µmol kg^{-1})	2606.90	2294.03	2250.40	1259.75	1967.30	689.10	1924.80	2241.95	1094.47	2370.85	2238.30
pH	8.01	7.17	7.80	6.60	7.71	6.57	7.70	8.03	7.06	8.00	7.37
CT (µmol kg^{-1})	2276.26	2384.64	2075.59	1662.79	1976.88	1043.02	1814.99	1912.94	1169.26	2042.30	2211.30
CO_2 (µmol kg^{-1})	12.97	123.80	20.88	404.50	44.67	354.80	23.47	9.99	86.51	11.47	59.08
CO_2 (% of C_T)	0.57	5.19	1.01	24.33	2.26	34.02	1.29	0.52	7.40	0.56	2.67
HCO_3^- (µmol kg^{-1})	2017.48	2235.60	1919.51	1257.05	1903.75	688.03	1700.60	1671.73	1075.14	1795.39	2093.00
HCO_3^- (% of C_T)	88.63	93.75	92.48	75.60	96.30	65.96	93.70	87.39	91.95	87.91	94.65
CO_3^{2-} (µmol kg^{-1})	245.80	25.24	135.20	1.24	28.46	0.20	90.91	231.22	7.62	235.44	59.22
CO_3^{2-} (% of C_T)	10.80	1.06	6.51	0.07	1.44	0.02	5.01	12.09	0.65	11.53	2.68
pCO_2 (µatm)	510.71	4442.31	779.01	13534.06	1569.81	10770.11	904.23	400.39	2899.52	460.77	2276.32
ΩCa	6.21	0.72	3.31	0.04	0.92	0.00	2.38	5.65	0.13	5.71	1.45

Source: own authorship.

The only possible biological effect on CO_2 content observed for 2019 campaigns was found for JE, between April 8th and May 17th, when a pH decrease from 8.01 to 7.17 was associated with a bloom of phytoplanktonic community (Chl-*a* = 30.58 mg m^3, Table 2). This trend is in agreement with previous studies in eutrophic estuaries (ABRIL *et al.*, 2003; LEOPOLD *et al.*, 2016), but in disagreement with the research of Cotovicz *et al.* (2015) that reported the Guanabara Bay as a CO_2 sink due to photosynthetic activities. In our work, the net heterotrophy (DO = 1.77 mL L^{-1}) in JE induced by eutrophication and secondary production (thus higher respiration rates) along with lower buffering capacity (A_T drop from 2606.9 µmol kg^{-1} to 2294 µmol kg^{-1}) caused by greater estuarine water domination (S from 30.7 to 16.8) was sufficient to acidify and oversaturate the system with respect to CO_2 (pCO_2 = 4442.3 µatm). Additionally, higher values of NO_2^- (an intermediate compound of the nitrification) and

NO_3^- (final product of nitrification) observed for the same sampling campaign suggest that nitrification, an aerobic process, could also explain the lowest A_T, pH and DO concentrations of JE samples by producing free protons and consuming DO, leading to decreased buffering capacity of CO_2 and its increased contents.

Estuarine waters were oversaturated in almost all samples from 2019, as their pCO_2 values were very high, and possibly represent a CO_2 source to the atmosphere (Table 3). SE posed the only exception, in May 17th, when pCO_2 was 400.4 µatm and close to the atmospheric pCO_2 of 409.95 µatm (NOAA, 2019). Highest values of pCO_2 (13534.1 µatm and 10770.1 µatm) were found in the most acidic waters of IPE, where water buffering capacity was not strong enough for neutralizing its high CO_2 production. As a consequence of strong oversaturation of CO_2, carbonate concentrations (0.2 – 28.5 µmol kg^{-1}) were low and consequently so were calcite saturation values ($\Omega Ca = 0 – 0.92$) for all samples of IPE and one sample from JE (May 17th) and SE (July 5th) (Table 3). According to the studies of Jonge & Villerius (1989), calcite is an important component of phosphate transport in estuarine environments. It tends to adsorb onto calcite, and, once this compound reaches the upper estuary, the calcite dissolution makes some of the phosphate desorb. There, the released phosphate tends to readsorb onto suspended materials such as clay minerals and iron oxyhydroxide, which are carried back to the estuarine environment. Thus, this process favors phosphate retention in the estuaries' middle reaches. In our study, low values of phosphate (0.43 – 3.18 µmol kg^{-1}) in IPE station suggests this compound undergoes such mechanism in the upper reaches of the IPE.

An important reconsideration is necessary regarding CO_2 system parameters among some of the studied sites, specially the innermost. As discussed by several authors, pCO_2 calculated data from A_T-pH are prone to overestimation and could be in average 2710 µatm higher than the measured pCO_2 for samples with pH of 6-7 (ABRIL *et al.*, 2015). The same study attributed this trend possibly to lower buffering capacity of acidic waters and/or significant dissolved organic carbon (DOC) contribution to A_T, the latter also reported in previous works (KIM *et al.*, 2006; KO *et al.*, 2016; LEOPOLD *et al.*, 2016). By comparing A_T with A_{inorg} for all samples (Table 3), very low differences (ΔA = -0.27 to -0.069 µmol kg^{-1}) between these two variables were observed for the previously mentioned undersaturated samples with respect to calcite (JE, IPE and SE).

Table 3 - Measured and calculated alkalinity for esturine systems studied in 2019. All alkalinity values are expressed in µmol kg^{-1}.

	JE			**IPE**			**SE**			**FE**	
	04/08	**05/17**	**07/05**	**04/08**	**05/17**	**07/05**	**04/08**	**05/17**	**07/05**	**05/17**	**07/05**
A_T	2606.900	2294.030	2250.400	1259.750	1967.300	689.100	1924.800	2241.950	1094.467	2370.850	2238.300
A_{carb}	2509.086	2286.085	2189.913	1259.524	1960.671	688.421	1882.431	2134.159	1090.375	2266.266	2211.446
A_B	80.349	5.840	54.090	0.149	2.386	0.006	36.393	96.307	2.983	94.486	24.362
A_{OH}	9.133	0.840	4.598	0.106	1.669	0.049	4.057	10.194	0.476	9.572	1.928
A_P	5.109	0.846	1.385	0.200	0.947	0.798	0.535	0.330	0.114	0.128	0.222
A_{Si}	3.233	0.487	0.431	0.021	1.646	0.096	1.404	0.969	0.608	0.408	0.386
A_{inorg}	2606.910	2294.099	2250.416	1260.002	1967.320	689.370	1924.820	2241.960	1094.556	2370.860	2238.344
ΔA	-0.010	-0.069	-0.016	-0.252	-0.020	-0.270	-0.020	-0.010	-0.089	-0.010	-0.044
pCO_2	510.71	4442.31	779.01	13534.06	1569.81	10770.11	904.23	400.39	2899.52	460.77	2276.32

Source: own authorship

These values were in discrepancy with the Baltic Sea, a DOC rich sea, that showed ranges of A_T and A_{org} of 790-1709 µmol kg^{-1} and 27-58 µmol kg^{-1} (KULIŃSKI *et al.*, 2014), as well with the works of Hernandez-Ayon *et al.* (2007) and Kim *et al.* (2006), that reported organic bases contribution to total alkalinity of greater than 50 µmol kg^{-1} and close to that of borate ion, respectively. JE, IPE and SE are marked by a mangrove domination along great extensions of their margins. Such biome is highly productive (ARREOLA-LIZÁRRAGA *et al.*, 2004; KOMIYAMA *et al.*, 2008) and could be a significant contributor of DOC to the system. Moreover, all three stations are near and used by the cities of Jaboatão, Ipojuca and Sirinhaém, possibly representing an additional sources of DOC and POC from direct OM input. Despite the coastal waters dominance for JE station, the observed phytoplankton bloom could be significantly contributing to A_T, as such organisms are reported to do so either by producing DOM (and thus A_{org}) during photosynthesis (KIM & LEE, 2009; KO *et al.*, 2016) or the presence of negatively charged surface groups on the phytoplankton cells that react with free protons (KIM *et al.*, 2006). Thus, it is reasonable to assume that calculations of CO_2 system parameters for such environments using the classic model of A_T could be overestimating A_{inorg} (mainly due to A_{carb} overestimation), once ΔA should be but is not sufficient to represent the presumably great A_{org} influence. Lastly, in order to better understand the processes and extent of miscalculations regarding the water buffering capacity in DOC rich environments, it is essential to make direct measured C_T and pCO_2, as well for DOC information, along with the data discussed in this work.

4 CONCLUSIONS

A notable heterogeneity of controlling processes in terms of CO_2 dynamics was observed along the studied estuarine systems. Dilution effect is an important regulator as carbonate-rich marine waters are capable to neutralize to some degree high CO_2 content from riverine discharge. However, biogeochemical processes could prevail in regulating CO_2 system parameters in urbanized estuaries due to pollution by human activities. The Capibaribe river and Jaboatão river lower estuaries had aerobic consumption of organic matter and eutrophication processes counterbalancing seasonal and tidal effect on their buffering capacity for the former, and buffering capacity, CO_2 content and pH for the latter. The Santa Cruz Channel presented considerable resilience under increased human intervention over the recent years, which is reflected by the great influence of dilution effect over total alkalinity variabilities. Furthermore, the Jaboatão river, Sirinhaém river and Formoso river estuaries, as well the Ipojuca river upper estuary were oversaturated with respect to CO_2 and behave as sources of this gas to the atmosphere under different weather conditions and tidal stages. As expected, the oligohaline and freshwaters of the upper estuary of Ipojuca river were the strongest sources, where low buffering capacity is not sufficient for neutralizing its great CO_2 content. However, pCO_2 calculated data is prone to overestimation due to lack of accounting for organic alkalinity contribution to buffering capacity by seawater models and needs to be better assessed with direct measurements of pCO_2, dissolved inorganic and organic carbon. The observed oversaturation state and potential organic buffering capacity both emphasize the importance of further studies in such environments, as they could contribute to more accurate descriptions of CO_2 system dynamics in tropical estuaries. Furthermore, the detected pollution effects over the CO_2 system suggests that those studies should also assess the potential effects of pollution on such system, as they could contribute with new arguments to the implementation of mitigation policies on this issue by local decision makers.

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