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# Nutrient Input and CO<sub>2</sub> Flux of a Tropical Coastal Fluvial System with High Population Density in the Northeast Region of Brazil

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## ABSTRACT

The carbon dioxide flux through the air-water interface of coastal freshwater ecosystems must be quantified to understand the regional balances of carbon and its transport through coastal and estuarine regions. The variations in air-sea CO<sub>2</sub> fluxes in nearshore ecosystems can be caused by the variable influence of rivers. In the present study, the amount of carbon emitted from a tropical coastal river was estimated using climatological and biogeochemical measurements (2002-2010) obtained from the basin of the Capibaribe River, which is located in the most populous and industrialized area of the northeast region of Brazil. The results showed a mean CO<sub>2</sub> flux of +225 mmol·m<sup>-2</sup>·d<sup>-1</sup>, mainly from organic material from the untreated domestic and industrial wastewaters that are released into the river. This organic material increased the dissolved CO<sub>2</sub> concentration in the river waters, leading to a partial pressure of CO<sub>2</sub> in the aquatic environment that reached 31,000 μatm. The months of April, February and December (the dry period) showed the largest monthly means for the variables associated with the carbonate system (HCO<sub>3</sub><sup>-</sup>, DIC, CO<sub>2(aq)</sub>, CO<sub>3</sub><sup>2-</sup>, TA, temperature and pH). This status reflects the state of permanent pollution in the basin of the Capibaribe River, due, in particular, to the discharge of untreated domestic wastewater, which results in the continuous mineralization of organic material. This mineralization significantly increases the dissolved CO<sub>2</sub> content in the estuarine and coastal waters, which is later released to the atmosphere.

**Keywords:** Tropical River; Nutrient Load; CO<sub>2</sub> Flux; Anthropogenic Pollution; Freshwater Ecosystem Impact

## 1. Introduction

Rivers and estuaries play an important role in the transport and transformation of carbon from the continent to the adjacent coastal zone and typically act as liquid sources of CO<sub>2</sub> to the atmosphere [1-3]. Although approximately 60% of the global freshwater inputs and 80% of the total organic carbon occur at tropical and subtropical latitudes [4,5], the number of works that have quantified the air-water exchanges of CO<sub>2</sub> in tropical estuaries and rivers is still extremely limited [6].

Recent studies estimate that rivers supply 0.8 - 1.33 PgC to the oceans worldwide, of which ~0.53 PgC is transported from tropical rivers (30°N - 30°S) to adjacent estuarine systems [7]. Nearshore coastal systems, such as estuaries, saltmarsh waters, mangroves mangrove swamps, coral reefs, and coastal upwelling systems, generally act

as sources of CO<sub>2</sub>, and a preliminary analysis suggested that the overall emission of CO<sub>2</sub> from these systems could be as high as 0.40 PgC·yr<sup>-1</sup>, thus balancing the CO<sub>2</sub> sink associated with marginal seas [1,6]. A recent study [8] evaluated the exchange of CO<sub>2</sub> between inner estuaries and the atmosphere based on a compilation of 62 systems. The computed emission of +0.27 ± 0.23 PgC·yr<sup>-1</sup> given by this study is lower than previous estimates, which range between +0.36 and +0.60 PgC·yr<sup>-1</sup> [1,9,10]. However, all recent studies have shown higher values than the first reported estimations (0.1 PgC·yr<sup>-1</sup>) [11].

Most studies prior to 2005 covered estuaries that were located largely in the mid-to-high latitudes (mostly in Europe). Estuaries at the lower latitudes received less attention, although the total surface area of the low-latitude estuaries is larger than that of the estuaries in mid- and high-latitude systems [1]. According to [6], the av-

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average CO<sub>2</sub> effluxes from low-latitude (0° - 30°) and mid-latitude (30° - 60°) estuaries are 17 and 46 mol CO<sub>2</sub> m<sup>-2</sup>·yr<sup>-1</sup>, respectively. A recent study [12] reported an efflux of 13 mol CO<sub>2</sub> m<sup>-2</sup>·yr<sup>-1</sup> for a tropical estuary (the Piauí estuary, Brazil, latitude 10°S). As indicated by [6], the current calculation is based on a very limited data set from subtropical and tropical regions. Estimates of the variability in air-sea CO<sub>2</sub> fluxes on seasonal and interannual time scales in tropical estuaries are necessary to help constrain the net partitioning of CO<sub>2</sub> between the atmosphere, oceans and terrestrial biosphere.

In Brazil, and particularly in the northeastern region of the country, very little is known about the seasonal and interannual variability of the CO<sub>2</sub> flux at the air-water interface in rivers, and even less is known about its long-term evolution given the increase of atmospheric CO<sub>2</sub>.

According to [13,14], the interannual variations of air-sea CO<sub>2</sub> fluxes in nearshore ecosystems can be caused by a variable river influence. The chemical processes that involve fluvial carbon are intimately associated with the organic and inorganic forms of carbon and their atmospheric and lithological origins [15]. Thus, quantifying the CO<sub>2</sub> flux through the air-water interface of freshwater ecosystems is necessary to understand regional carbon balances and the relative contributions of these systems to the planetary increase of atmospheric CO<sub>2</sub>.

The objective of the present study was to characterize and quantify the seasonal and interannual variability of CO<sub>2</sub> fluxes and the variables associated with the carbonate system in a tropical river that is located in a high-population-density urban area. The Capibaribe River was selected because it is highly representative based on the large number of tropical coastal systems in Brazil and throughout the world that experience high anthropogenic pressure. The waters of the Capibaribe River are subjected to an intense eutrophication process [16], resulting mainly from its proximity to the Metropolitan Region of Recife (from now on referred to as RMR—Região Metropolitana do Recife), the most populous and industrialized area in northeastern Brazil

## 2. Methodology

### 2.1. Study Area

The hydrographic basin of the Capibaribe River covers 7557.42 km<sup>2</sup> and is located in the coastal region of the State of Pernambuco, Brazil (**Figure 1**). Lithologically, the Capibaribe River basin is composed of 90% crystalline basement and 10% sedimentary basin. In the lower Capibaribe River, near the MRR, the Tertiary-aged Barreiras formation is represented by disperse sedimentary deposits that indistinctly cover the crystalline basement and the sedimentary basin. Natural vegetation covers 56.3% of the total drainage area of the Capibaribe River,

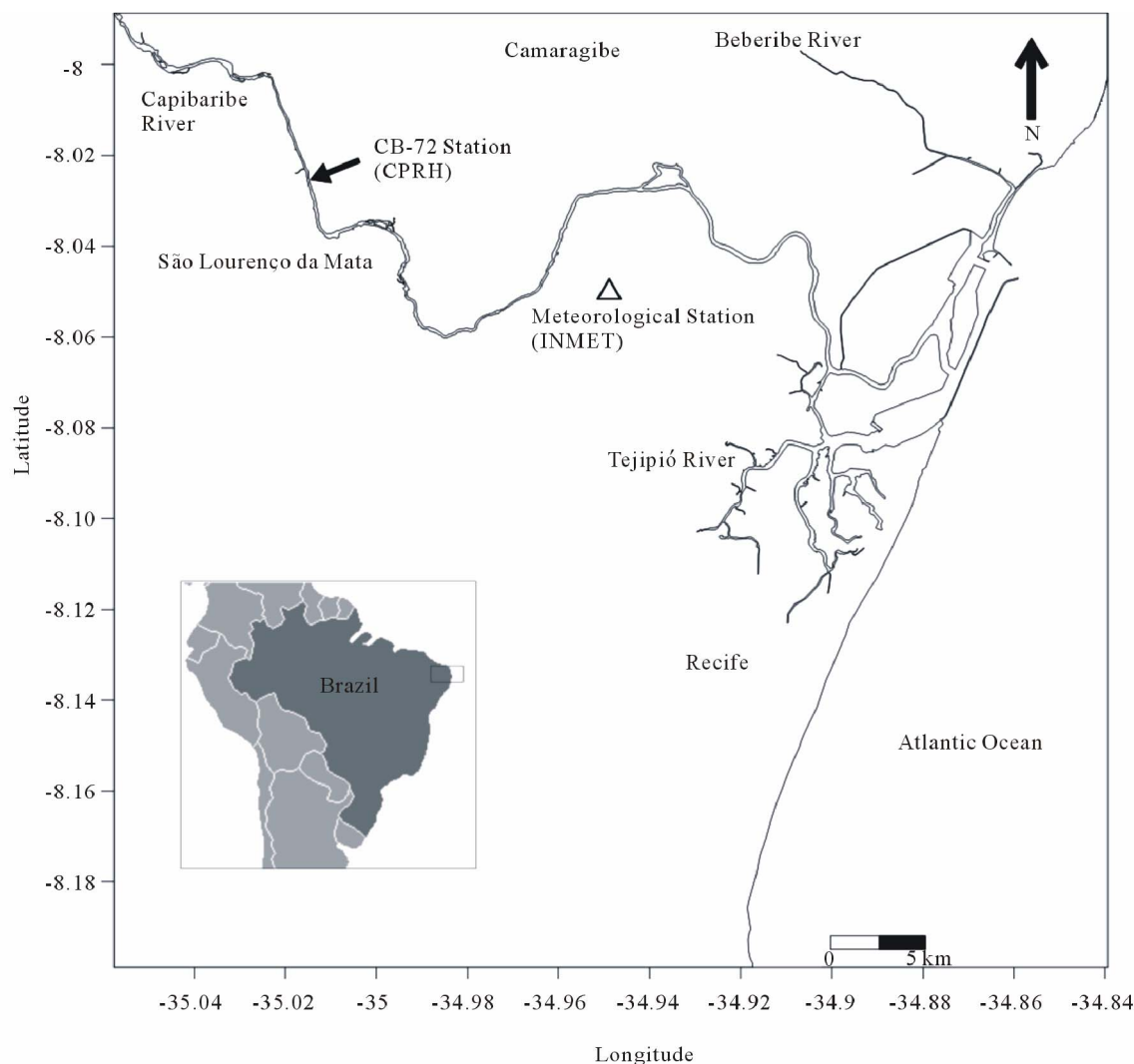
with 38.8% represented by agricultural areas, 3.14% attributed to urban areas and 0.45% occupied by the continental water body [17]. Given its wide geographical coverage, the Capibaribe basin exhibits a complex environment that is characterized by climatic contrasts in the terrain, soils and vegetation cover and marked socioeconomic gradients. From its headwaters, located 240 km from the coastline, to its mouth in the MRR, the river crosses 42 municipalities, of which 15 are completely comprised within the basin, and 26 have their administrative center in this basin [17]. The total population of the basin is 1,450,000 inhabitants [18,19], for a mean population density in the basin of 190 inhabitants km<sup>-2</sup>, with the highest concentration in the MRR (1000 inhabitants km<sup>-2</sup>).

Various activities occur in the basin, and the main activities include the production of food, non-metallic minerals, textiles, metallurgy, chemicals, pharmaceutical products, veterinary products, sugars/ethanol, leathers, plastic materials, drinks, transport materials and wood. The residual organic load that effectively reaches the body of water is estimated at 32.4 t biochemical oxygen demand (BOD) day<sup>-1</sup>, of which 95.7% is of domestic origin and 4.3% is of industrial origin [19]. Furthermore, according to [17], the residual organic load can reach values of up to 28 t BOD day<sup>-1</sup> at collection station CB-72/CPRH (**Figure 1**).

### 2.2. Climatology and Fluvial Discharge

The Capibaribe River basin exhibits a high spatial variability in precipitation, with mean annual values between 600 mm and 2400 mm (mean = 1133 mm from 1990 to 2010), with an increase in precipitation closer to the coast. This spatial variability reflects the influence of the two main atmospheric systems that affect the eastern edge of the northeast region of Brazil, the Intertropical Convergence Zone and the Atmospheric Easterly Waves [17,20]. Potential evapotranspiration is approximately 1700 mm, with a decrease near the coast, where the value falls to 1500 mm.

The mean annual temperature in the Capibaribe River basin varies between 20.4°C and 26.1°C, while the maximum temperature oscillates between 25.5°C and 29.9°C. Throughout the year, the temperatures in the region display a variability that can be represented by two seasons: a period with lower monthly means between April and September and the period from October to March, during which the mean temperature values increase. The winds vary between 2 m·s<sup>-1</sup> and 5 m·s<sup>-1</sup>, with the months of August, September and December displaying the highest monthly wind speeds [21]. The mean fluvial discharge in the São Lourenço da Mata station (**Figure 1**) is 13.74 m<sup>3</sup>·s<sup>-1</sup>, resulting in a specific flow



**Figure 1.** Capibaribe River Basin with the location of sampling station CB-72 (CPRH—Pernambuco State Environmental Agency) and the Várzea Meteorological Station (INMET—Brazilian National Institute of Meteorology).

rate of  $9.79 \text{ L}\cdot\text{s}^{-1}\cdot\text{km}^{-2}$  [17].

In the present study, the climatological and fluvial discharge variables were analyzed using a historical time series of 20 years (1990-2010), with a special focus on the period that included biogeochemical and river water quality data (2002-2010). These last data were sampled and analyzed bimonthly from 2002-2010 at Station CB-72 (**Figure 1**), which is under the responsibility of the State Agency of the Environment and Water Resources (Agência Estadual de Meio Ambiente e Recursos Hídricos—CPRH) [19]. As will be discussed later, the statistical significance between these two series of physical data (climatology and river flow) was assessed to detect trends and verify the climatological representativeness of the performed analyses for 2002 to 2010, for which river water quality data were available, making the simultaneous use of physical and biogeochemical data

possible.

The fluvial discharge values were obtained from the database of the National Water Agency of Brazil (Agência Nacional de Águas—ANA) [22], while the data on air temperature and pluviometric precipitation were obtained from the Brazilian National Institute of Meteorology (Instituto Nacional de Meteorologia—INMET) [21].

The historical series of evaporation data was obtained from the Department of Water Resources (Secretaria de Recursos Hídricos—SRH) [17], and the evapotranspiration rate was determined as follows using the Hargreaves method [23] and data on the latitude, air temperature and relative humidity:

$$\text{EVTP}(i) = \text{FL} \times (32 + 1.8 \times \text{TEMP}) \times 0.158 \times (100 - \text{HU})^{0.5} \quad (1)$$

where  $\text{EVTP}(i)$  = Hargreaves' potential evapotranspira-

tion for month “ $i$ ” (mm); FL = factor latitude (calculated as in [23]); TEMP = monthly mean temperature ( $^{\circ}\text{C}$ ); and HU = mean monthly relative humidity (%).

### 2.3. Air-Water $\text{CO}_2$ Flux

The air-water  $\text{CO}_2$  flux was determined based on bi-monthly measurements (2002 to 2010) of pH, temperature, salinity and alkalinity that were obtained at station CB-72 of the CPRH in combination with climatological data (precipitation, wind intensity and atmospheric pressure) from the Meteorological Station of INMET (Figure 1).

The dissolution constants for carbonic acid that were used in the calculations were obtained from [24] for salinities of 0.1 - 50 and temperatures of  $1^{\circ}\text{C}$  -  $50^{\circ}\text{C}$ . The  $\text{CO}_2$  solubility coefficient was calculated using the equations in [25], and the dissociation constants of sulfate [26] and borate [27] were calculated as follows:

$$FCO_2 = k(\text{CO}_2) \times KH \times \Delta p\text{CO}_2 \quad (2)$$

where  $FCO_2 = \text{CO}_2$  flux at the air-water interface ( $\text{mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ );  $k(\text{CO}_2)$  = gas-transfer rate ( $\text{m} \cdot \text{s}^{-1}$ );  $KH$  =  $\text{CO}_2$  solubility, calculated according to [25] ( $\text{m} \cdot \text{L}^{-1} \text{atm}^{-1}$ ); and  $\Delta p\text{CO}_2$  = difference between the partial pressure of  $\text{CO}_2$  on the water surface ( $p\text{CO}_{2(\text{aq})}$ ) and in the atmosphere ( $p\text{CO}_{2(\text{air})}$ ) ( $\mu\text{atm}$ ).

A positive value of  $\Delta p\text{CO}_2$  indicates a liquid flux of water to the atmosphere. The partial pressure of atmospheric  $\text{CO}_2$  was obtained through the following equation:

$$p\text{CO}_{2(\text{air})} = p\text{CO}_2 = x\text{CO}_{2\text{atm}} \times (P_{\text{atm}} - p\text{H}_2\text{O}) \quad (3)$$

where  $P_{\text{atm}}$  = barometric pressure, obtained from the local meteorological data (atm);  $x\text{CO}_2$  = mole fraction of atmospheric  $\text{CO}_2$ , obtained from NOAA (<http://esrl.noaa.gov>) (ppm); and  $p\text{H}_2\text{O}$  = water vapor pressure ( $\mu\text{atm}$ ), obtained from [28].

The water vapor pressure was determined using the following equation:

$$p\text{H}_2\text{O} = e^{\left(24.4543 - 67.4509 \times \left(\frac{100}{\text{sst}}\right) - 4.8489 \times \ln\left(\frac{\text{sst}}{100}\right) - 0.000544 \times S\right)} \quad (4)$$

where  $\text{sst}$  = the sea surface temperature of the body of water ( $^{\circ}\text{K}$ ) and  $S$  = the salinity of the body of water.

The gas-transfer rate was calculated using the equation from [29] as follows:

$$k(\text{CO}_2) = 1.91 \times \exp(0.35 \times (u_{10})) \times (Sc/600)^{-0.5} \quad (5)$$

where  $u_{10}$  is the wind speed at 10 m from the surface of the body of water ( $\text{m} \cdot \text{s}^{-1}$ ) and  $Sc$  is the Schmidt number.

The results obtained from Equations (2)-(5), combined with the results from the analyses of the mineral nutrients [19], were used as input data for the  $\text{CO}_2$  calc<sup>®</sup> software [30]. This software uses the equations of the carbonate

system to obtain  $p\text{CO}_2$  in the water,  $\text{HCO}_3^-$ ,  $\text{CO}_2$  aqueous,  $\text{CO}_3^{2-}$ , dissolved inorganic carbon (DIC) and other parameters derived from the carbonate system.

The excess of  $\text{CO}_2$  ( $\text{CO}_{2(\text{aq})}$ ) ( $\mu\text{mol} \cdot \text{kg}^{-1}$ ) is defined as the amount of DIC that is transferred as  $\text{CO}_2$  to the atmosphere after attaining air-water equilibrium. The excess of  $\text{CO}_2$  was calculated according to the equation from [31], as follows:

$$\text{CO}_{2(\text{aq})} = \text{Exc. CO}_2 = [\text{CO}_2^*] - K_{\text{H}}^{\text{CO}_2} \times p\text{CO}_{2(\text{air})} \quad (6)$$

where  $[\text{CO}_2^*]$  is the concentration of total free  $\text{CO}_2$  in  $\mu\text{mol} \cdot \text{kg}^{-1}$  (i.e.,

$[\text{CO}_2^*] = [\text{CO}_2] + [\text{H}_2\text{CO}_3] = \text{KHCO}_3 \times p\text{CO}_2$  in water) and  $K_{\text{H}}^{\text{CO}_2}$  is the solubility coefficient of  $\text{CO}_2$ .

The apparent oxygen utilization (AOU,  $\mu\text{mol} \cdot \text{kg}^{-1}$ ) was determined based on the equation in [32]:

$$\text{AOU} = (\text{O}_2)_{\text{eq}} - (\text{DO}\%) \quad (7)$$

with the dissolved oxygen saturation ( $\%\text{O}_2$ ) calculated according to the following equation:

$$(\text{DO}\%) = (\text{O}_2/\text{O}_2^*) \times 100 \quad (8)$$

where  $[\text{O}_2]_{\text{eq}}$  = the dissolved oxygen (DO) concentration at equilibrium with the atmosphere, calculated based on [33] and the local air pressure ( $\mu\text{mol} \cdot \text{kg}^{-1}$ );  $[\%\text{O}_2]$  = DO saturation (%);  $\text{O}_2 = \text{in situ}$  DO concentration ( $\mu\text{mol} \cdot \text{kg}^{-1}$ ); and  $\text{O}_2^*$  = solubility of oxygen as a function of temperature and salinity ( $\mu\text{mol} \cdot \text{kg}^{-1}$ ).

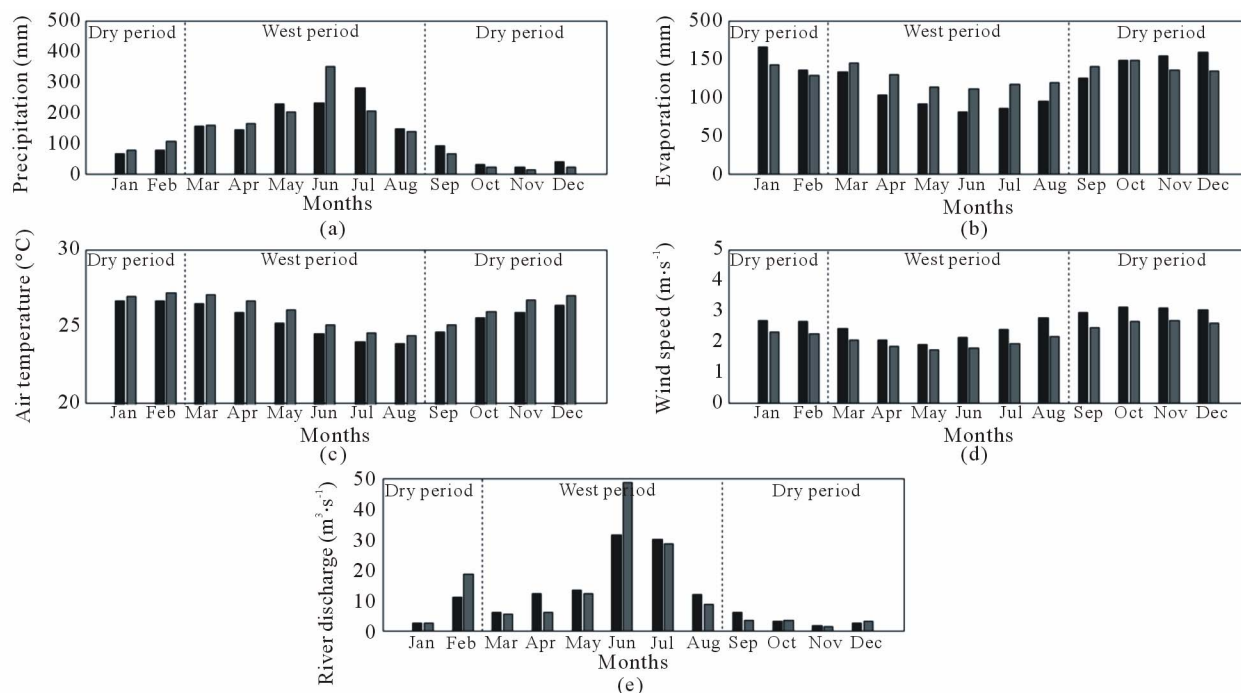
The statistical analyses (t-test, trend, PCA and descriptive statistics) were performed using XLSTAT<sup>®</sup> 2010 software. The non-parametric Mann-Kendall test was selected, which is widely utilized to detect monotonic trends in data series, without the need to specify whether these trends are linear.

## 3. Results

### 3.1. Climatology and Fluvial Discharge

The air temperature, pluviometric precipitation and evaporation did not show significant differences between the historical period (1990-2010) and the study period (2002-2010) (t-test;  $\alpha = 0.05$ ) (Figures 2(a)-(c)). The annual water balance was positive, with a seasonal variability characterized by 6 months of positive water balance (March to August) and 6 months of negative water balance (September to February). According to the Mann-Kendall trend test ( $\alpha = 0.05$ ), the observed data on precipitation, temperature and humidity did not show significant increasing or decreasing trends for these variables.

Fluvial discharges did not show significant differences between the historical period and the study period (t-test;  $\alpha = 0.05$ ) (Figure 2(e)). The mean flow rate for the study



**Figure 2.** Seasonal variability in the Capibaribe River basin, Brazil, calculated based on the historical time series 1990-2010 (black bars) and the period 2002-2010 (gray bars): (a) Precipitation; (b) Evaporation; (c) Air temperature; (d) Wind speed and (e) Fluvial discharge. Wet period = March-August, dry period = September-February.

period was  $11.8 \text{ m}^3 \cdot \text{s}^{-1}$ , which was very similar to the value of  $13.7 \text{ m}^3 \cdot \text{s}^{-1}$  obtained for the historical period (1990-2010) [17]. Based on the Mann-Kendall test ( $\alpha = 0.05$ ), there was no significant trend (increasing or decreasing) in the flow rate data from 1990-2010.

The wind intensities show significant differences between the historical period and the study period ( $t$ -test;  $\alpha = 0.05$ ). The mean annual value recorded in the period from 2002-2010 of  $2.2 \text{ m} \cdot \text{s}^{-1}$  was lower than the historical mean value of  $2.6 \text{ m} \cdot \text{s}^{-1}$ . All of the monthly wind intensities were lower than those recorded historically in the region (**Figure 2(d)**). Based on the Mann-Kendall test ( $\alpha = 0.05$ ;  $p < 0.0001$ ), there was a positive (growing) trend among the historical wind data (1990-2010).

### 3.2. Water Temperature, Salinity, Organic Load (BOD) and Dissolved Oxygen (DO%)

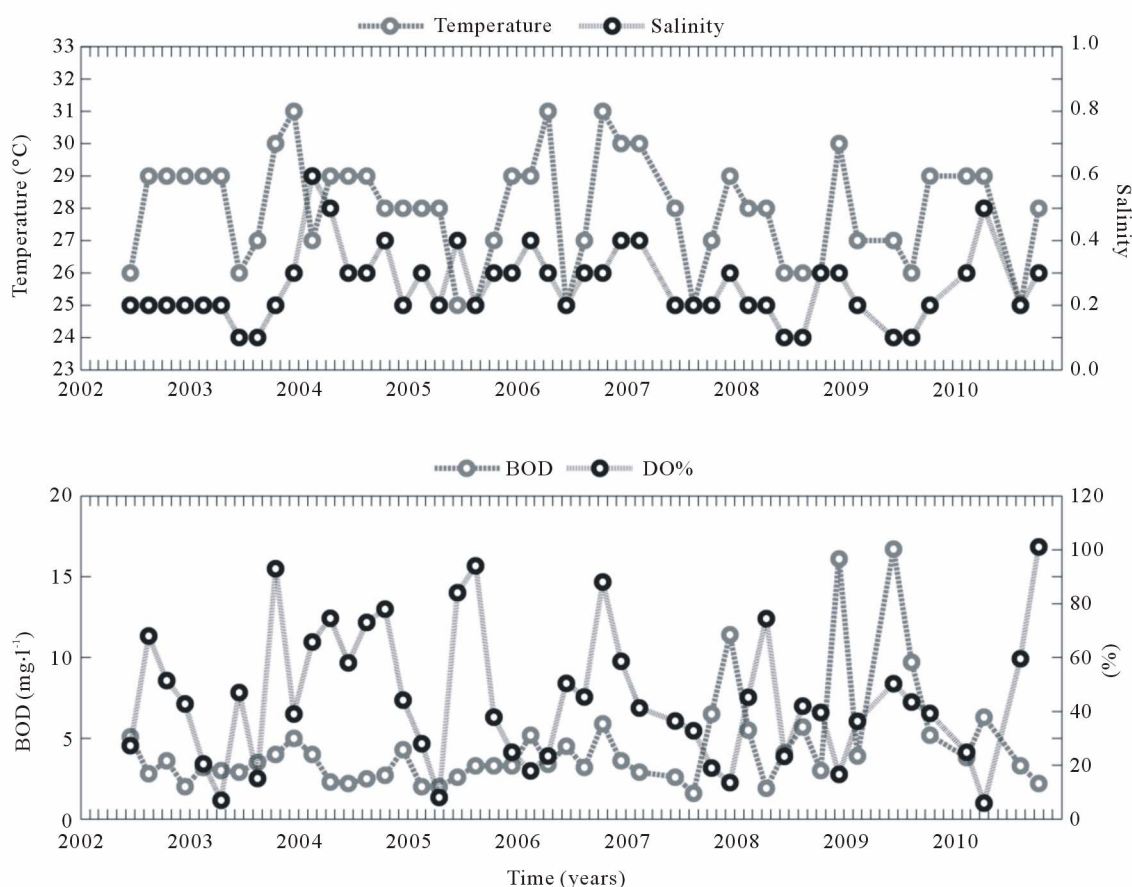
Water temperature and salinity did not show significant trends according to the Mann-Kendall test ( $\alpha = 0.05$ ), indicating the repetitive cyclical nature of these state variables in the study period. The coefficient of variation for both state variables was minimal (0.1 and 0.4, respectively). According to the  $t$ -test ( $\alpha = 0.05$ ;  $p < 0.002$ ), the mean seasonal water temperatures (March-August x September-February) showed significant differences between the wet and dry periods of the year. The amplitude of the means was  $1.5^\circ\text{C}$  (wet =  $27.1^\circ\text{C}$  and dry =  $28.6^\circ\text{C}$ ).

The mean salinity value was  $0.3 \pm 0.01$  units, with

maximum values in February (dry period) and minimum values in June (wet period), indicating that salinity follows the climatic seasonal cycle. The salinity in this section of the river was classified as freshwater (94% of the values were  $<0.5$ ).

The mean BOD concentration was  $4.4 \pm 3 \text{ mg} \cdot \text{l}^{-1}$  from 2002-2010. When this concentration was associated with fluvial discharge, a mean input of  $53.1 \text{ t BOD} \cdot \text{d}^{-1}$  in the Capibaribe River was obtained, which represents 63.8% more than the residual pollution load that was reported by the CPRH for 2010 ( $32.4 \text{ t BOD} \cdot \text{d}^{-1}$ ). The data observed do not show significant differences ( $\alpha = 0.05$ ;  $p < 0.9$ ) in the mean concentrations of organic load between the dry and wet periods. The data series for the BOD concentration of the period 2002-2010 showed a maximum value of  $16.7 \text{ mg} \cdot \text{l}^{-1}$  and a minimum of  $0.5 \text{ mg} \cdot \text{l}^{-1}$  (**Figure 3(b)**). Values above  $5 \text{ mg} \cdot \text{l}^{-1}$  are above the legal limit recommended by the Brazilian legislation for this type of water source [34]. According to the Mann-Kendall test, there is a positive trend in the BOD data ( $\alpha = 0.05$ ;  $p < 0.025$ ), indicating a gradual increase in the levels of biodegradable organic material during the study period.

The dissolved oxygen saturation (DO%) showed a mean value of  $44\% \pm 20\%$ , with a mean DO concentration of  $(95 \pm 70 \mu\text{mol} \cdot \text{kg}^{-1})$  ( $3.04 \pm 2 \text{ mg} \cdot \text{l}^{-1}$ ) during 2002-2010. The highest monthly mean was recorded in October (during the dry period), while the lowest value was observed in April (during the wet period) (**Figure 3(b)**).



**Figure 3. Water temperature, salinity, biochemical oxygen demand (BOD) and saturation of dissolved oxygen (DO%) in the Capibaribe River, Brazil.**

Values less than  $5 \text{ mg}\cdot\text{l}^{-1}$  are below the limit recommended by the Brazilian legislation [34]. During the study period, 78% of the samples exhibited concentrations below this limit ( $5 \text{ mg}\cdot\text{l}^{-1}$ ).

According to the t-test ( $\alpha = 0.05$ ;  $p < 0.25$ ), the data did not show significant differences between the dry and rainy periods. Based on the Mann-Kendall test, the DO% did not show significant alteration trends ( $\alpha = 0.05$ ) from 2002-2010.

### 3.3. Dissolved Inorganic Carbon (DIC), Total Alkalinity (TA), pH and Mineral Nutrients ( $\text{PO}_4^-$ and $\text{NH}_4^+$ )

The DIC concentration during 2002-2010 showed a smaller variation than the other parameters associated with the carbonate system ( $596$  to  $2,235 \text{ }\mu\text{mol}\cdot\text{kg}^{-1}$ ; coefficient of variation = 0.2) (Figure 4(a)). The data did not show significant differences ( $\alpha = 0.05$ ;  $p < 0.2$ ) between the dry and rainy periods. Based on the Mann-Kendall test ( $\alpha = 0.05$ ), the DIC did not show a positive trend during 2002-2010, suggesting a continuous input of carbon inorganic species throughout the years. The mean

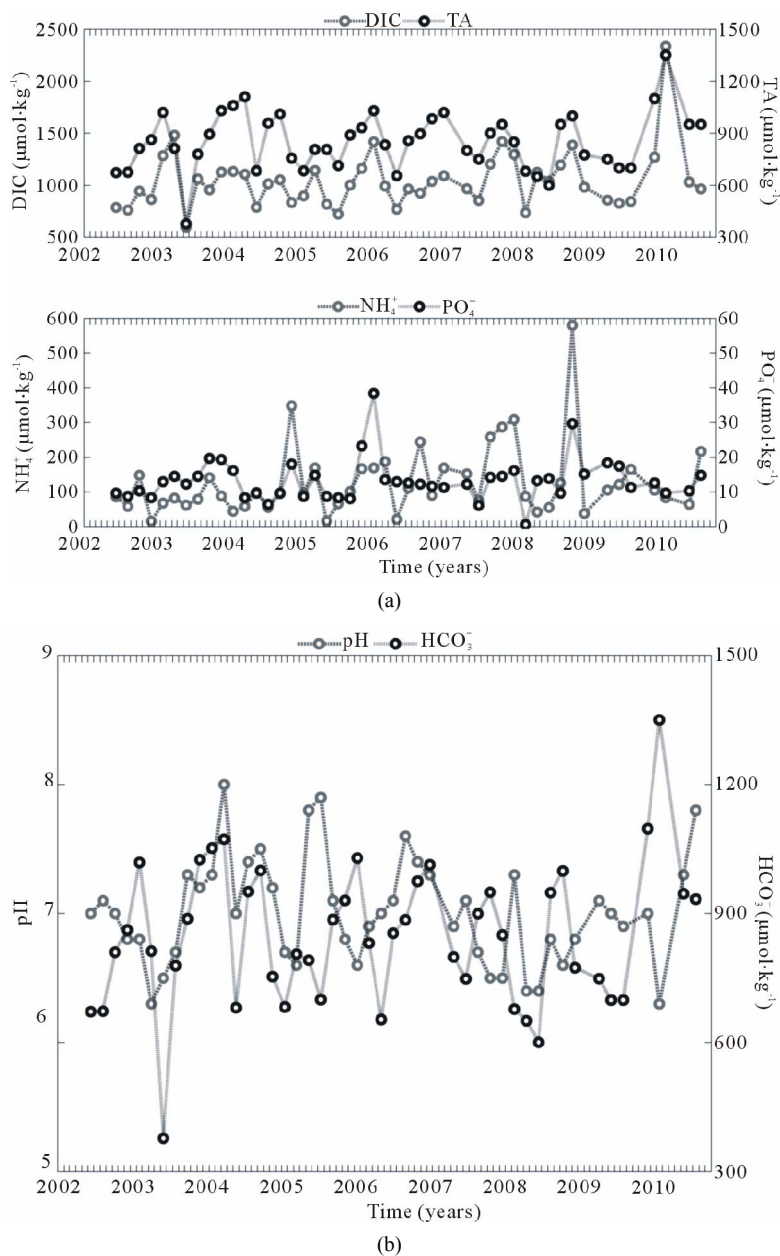
distribution of the compounds that comprise DIC was as follows:  $\text{HCO}_3^- = 80.8\%$ ;  $\text{CO}_3^{2-} = 0.2\%$  and  $\text{CO}_{2(\text{aq})} = 19\%$  (Table 1). Of these compounds,  $\text{CO}_3^{2-}$  and  $\text{CO}_{2(\text{aq})}$  displayed a higher coefficient of variation and thus influence the variation of the DIC concentration in the Capibaribe River.

The TA showed a mean value of  $851 \pm 160 \text{ }\mu\text{mol}\cdot\text{kg}^{-1}$  during 2002-2010 (Figure 4(a)). The estimated values showed significant differences between the dry and wet periods ( $\alpha = 0.05$ ;  $p < 0.004$ ), with a higher mean during the dry period ( $920 \text{ }\mu\text{mol}\cdot\text{kg}^{-1}$ ). The variance was  $377 - 1350 \text{ }\mu\text{mol}\cdot\text{kg}^{-1}$  (coefficient of variation = 0.2). Based on the Mann-Kendall test ( $\alpha = 0.05$ ), the TA did not show a positive trend during 2002-2010, indicating that the concentrations recorded in this period were constant. The highest monthly mean was observed in February ( $942 \text{ }\mu\text{mol}\cdot\text{kg}^{-1}$ ), while the lowest monthly mean TA occurred in June ( $674 \text{ }\mu\text{mol}\cdot\text{kg}^{-1}$ ).

The waters of the Capibaribe River show high concentrations of mineral nutrients that serve as important fertilizers in the adjacent estuarine and coastal waters [16]. The  $\text{PO}_4^-$  and  $\text{NH}_4^+$  concentrations measured during

**Table 1. Variables associated with the carbonate system in the Capibaribe River, Brazil, during 2002-2010. Mean values in parentheses represent the proportion (%) of the total DIC.**

Parameter	Descriptive Statistics		
	Mean $\pm$ SD	Maximum - Minimum	Coefficient of variation
Water temperature ( $^{\circ}$ C)	$27.9 \pm 1.7$	31 - 25	0.1
pH	$7.0 \pm 0.4$	8.0 - 6.3	0.1
$\text{FCO}_2$ ( $\text{mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ )	$+225 \pm 201$	+995 - +4.9	1.0
$p\text{CO}_2$ ( $\mu\text{atm}$ )	$8340 \pm 7300$	31,400 - 311	0.8
DIC ( $\mu\text{mol} \cdot \text{kg}^{-1}$ )	$1043 \pm 279$	2335 - 596	0.2
$\text{HCO}_3^-$ ( $\mu\text{mol} \cdot \text{kg}^{-1}$ )	$847 \pm 160$ (80.0%)	1350 - 377	0.2
$\text{CO}_3^{2-}$ ( $\mu\text{mol} \cdot \text{kg}^{-1}$ )	1.8	1.3 - 0.1	1.5
$\text{CO}_{2(\text{aq})}$ ( $\mu\text{mol} \cdot \text{kg}^{-1}$ )	$199 \pm 180$ (19.0%)	985 - 15.3	0.9



**Figure 4. (a) Concentration of dissolved inorganic carbon (DIC), total alkalinity (TA), ammonia ( $\text{NH}_4^+$ ) and orthophosphate ( $\text{PO}_4^-$ ) in the Capibaribe River, Brazil; (b) pH and concentration of bicarbonate ( $\text{HCO}_3^-$ ) in the Capibaribe River, Brazil.**



2002-2010 were above the corresponding limits recommended by the legislation [34]. The period from October to February (the dry period) systematically showed the highest concentrations of dissolved nutrients, reaching  $38 \mu\text{mol}\cdot\text{kg}^{-1}$  for  $\text{PO}_4^-$  and  $580 \mu\text{mol}\cdot\text{kg}^{-1}$  for  $\text{NH}_4^+$  (Figure 4(a)).

The pH values measured in the Capibaribe River did not show significant differences ( $\alpha = 0.05$ ;  $p < 0.9$ ) between the wet period and the dry period. The mean of the series was  $7.0 \pm 0.4$ ; however, low values were observed in both climatic periods (Figure 4(b) and Table 1).

The  $\text{HCO}_3^-$  concentrations showed significant differences ( $\alpha = 0.05$ ;  $p < 0.04$ ) between the wet and the dry period (Figure 4(b) and Table 1).

### 3.4. Partial Pressure of $\text{CO}_2$ in the Water ( $p\text{CO}_{2(\text{aq})}$ ) and $\text{CO}_2$ Flux ( $\text{FCO}_2$ )

The partial pressure of carbon dioxide in the Capibaribe River was highly variable throughout the study period (coefficient of variation = 0.8), ranging between 311 and  $31,400 \mu\text{atm}$ , with a mean value of  $8340 \mu\text{atm}$  (Figure 5(a) and Table 1). The  $p\text{CO}_{2(\text{aq})}$  values did not show significant differences between the dry and rainy periods ( $\alpha$

$= 0.05$ ;  $p < 0.6$ ). The highest monthly mean was recorded in April ( $17,440 \mu\text{atm}$ ) (Table 1). Based on the Mann-Kendall test ( $\alpha = 0.05$ ), the partial pressure of  $\text{CO}_2$  did not show a significant positive or negative trend during 2001-2010, indicating that the concentrations were consistent throughout the analyzed temporal series.

The progression of the  $\text{CO}_2$  flux ( $\text{FCO}_2$ ) in the Capibaribe River was always positive during the study period, with a mean value of  $+225 \text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ , indicating a continuous release of  $\text{CO}_2$  into the atmosphere (Figure 5(b)). The highest value calculated in the period was  $+995 \text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$  (April 2010), and the lowest flux was  $+4.9 \text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$  (August 2005), thus supporting the high coefficient of variation (Figure 5(b) and Table 1). Similarly to the water partial pressure, the  $\text{FCO}_2$  values did not show significant differences between the dry and rainy periods ( $\alpha = 0.05$ ;  $p < 0.5$ ). The highest monthly mean was also recorded in April ( $+426 \text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ), while the lowest monthly mean value was observed in August ( $+119 \text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ). Based on the Mann-Kendall test ( $\alpha = 0.05$ ), the  $\text{CO}_2$  fluxes did not show trends (positive or negative) during 2001-2010, indicating an almost continuous release to the atmosphere over the period analyzed.

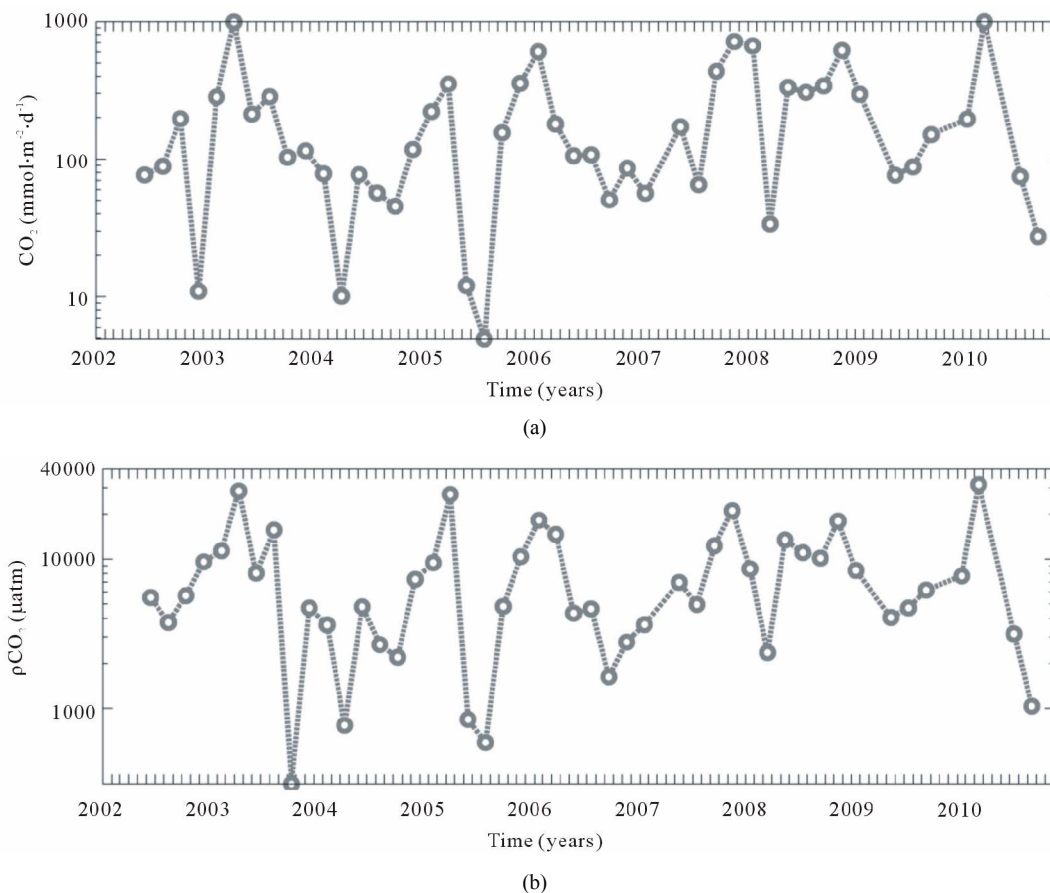


Figure 5.  $\text{CO}_2$  partial pressure in water ( $p\text{CO}_{2(\text{aq})}$ ) and  $\text{CO}_2$  water-air flux ( $\text{FCO}_2$ ) in the Capibaribe River, Brazil.

#### 4. Discussion

The processes that partition dissolved  $\text{CO}_2$ ,  $p\text{CO}_{2(\text{aq})}$  and DIC in fluvial environments are complex and influenced by a combination of sources and natural processes, such as the types of rock and soil in the hydrographic basin, water-atmosphere interaction and oxidation/reduction reactions of anthropogenic inputs [15]. Based on the results presented in the previous section, an analysis of the possible agents that influence the biogeochemistry and the carbon flux in the Capibaribe River, a typical tropical coastal system that is subjected to intense anthropogenic action in the northeast region of Brazil, will be presented next. The findings for the Capibaribe River reflect an important state of pollution in the drainage basin; this pollution is mainly due to the discharge of untreated domestic wastewater into the water. The estimated population density for 2010 in the city of Recife was 7000 inhabitants  $\text{km}^{-2}$ , and the mean density in the drainage basin reaches 191 inhabitants  $\text{km}^{-2}$  [18], resulting in a significant input of organic load that is released directly into the river [19].

When analyzing whether the type of rock/soil influenced the water  $\text{CO}_2$  content, no correlation between fluvial discharge and  $p\text{CO}_{2(\text{aq})}$  was observed ( $r^2 = 0.01$ ;  $p < 0.0001$ ) (**Figure 6(a)**), suggesting that the transport processes via fluvial runoff are not the main factors that are responsible for the high concentrations of dissolved  $\text{CO}_2$  found in the Capibaribe River. Authors such as [35] have shown that the lack of correlation between these two variables is characteristic of basins that are located in populous industrialized areas. For example, in the Zenne River (urban river in Brussels, Belgium), periods of high fluvial discharge were not correlated with high  $p\text{CO}_{2(\text{aq})}$  values [36].

Based on **Figure 6(b)** and **Table 2**, the BOD exhibited a low correlation with  $p\text{CO}_{2(\text{aq})}$  ( $r^2 = 0.04$ ); however, DO% showed a strong negative correlation with  $p\text{CO}_2$  ( $r^2 = 0.86$ ;  $p < 0.0001$ ; **Figure 6(b)**), indicating that the loads of domestic and industrial wastewaters increased during this period (2002-2010), thus increasing the organic matter decomposition and decreasing the pH (pH vs. DO%;  $r^2 = 0.70$ ;  $p < 0.0001$ ; **Figure 6(d)**). Additionally, the AOU was positively correlated with the excess of  $\text{CO}_{2(\text{aq})}$  ( $r^2 = 0.41$ ;  $p < 0.0001$ ; **Figure 6(e)**). This result indicates that the organic load that enters the Capibaribe River has a significant impact on the microbial processes that are associated with the carbon and nitrogen cycles. The nutrients enrich the water and can lead to an excessive production of algal biomass and, consequently, eutrophication. Thus, planktonic metabolism and the organic matter associated with domestic and industrial wastewaters can consume the dissolved oxygen in the water [16,37].

Nitrogen and phosphate compounds showed concentrations that are typical of bodies of water that are affected by urban inputs. The mean DIN (dissolved inorganic nitrogen) concentration was  $144 \mu\text{mol}\cdot\text{kg}^{-1}$ , while the ammonia concentration was  $134 \mu\text{mol}\cdot\text{kg}^{-1}$  (~90% of the DIN value). Simultaneously, the mean DIP (dissolved inorganic phosphate) concentration was  $13.2 \mu\text{mol}\cdot\text{kg}^{-1}$ . The DIN/DIP ratio was therefore 11:1, which is very similar to the ratio of 12:1 found by [38] for domestic and industrial waste waters; these compounds serve as a nutrient source for the microbial activity in many rivers [35]. High values of ammonium ( $\text{NH}_4^+$ ) and other nitrogen compounds ( $\text{NO}_3^-$  and  $\text{NO}_2^-$ ) in rivers and the processes associated with them, such as ammonification, nitrification and denitrification, have a strong and rapid effect on alkalinity. Under oxic conditions, ammonification produces  $\text{NH}_4^+$ , leading to  $\text{NO}_3^-$ . Under anoxic conditions, ammonification produces  $\text{NH}_4^+$ , and denitrification consumes  $\text{NO}_3^-$ . However, under both conditions, the changes in  $\text{NH}_4^+$  and  $\text{NO}_3^-$  affect the TA [39]. Thus, despite the high TA values observed in the Capibaribe River (mean =  $851 \pm 160 \mu\text{mol}\cdot\text{kg}^{-1}$ ), the analysis did not show a strong correlation between alkalinity and DO%,  $\text{NH}_4^+$  or  $p\text{CO}_{2(\text{aq})}$  (see **Figure 7** and **Table 2**).

According to [35], under conditions of high  $\text{CO}_{2(\text{aq})}$  values, which result from bacterial respiration, carbonic acid is produced and decreases the river water pH. If the characteristics of the body of water are such that the  $\text{CO}_2$  concentration in the aqueous media are close to equilibrium with atmospheric  $\text{CO}_2$ , strong correlations between alkalinity,  $p\text{CO}_{2(\text{aq})}$  and pH would be expected. However, the complex set of processes that lead to the production or consumption of  $\text{CO}_{2(\text{aq})}$  and the production or removal of carbonic acid ( $\text{HCO}_3^-$ ) prevent the establishment of a correlation between alkalinity, pH and  $p\text{CO}_{2(\text{aq})}$  [35,40]. These high alkalinity values may, therefore, be associated with the high values of  $\text{HCO}_3^-$  found in the Capibaribe River, which represent 81% of the total DIC, while  $\text{CO}_{2(\text{aq})}$  represents 19%, and the remainder (~0.2%) was associated with  $\text{CO}_3^{2-}$ . These values are in accordance with the values recorded for highly polluted rivers, including both tropical rivers, such as the Tietê [15] and Piracicaba [41] rivers of Brazil, and temperate rivers, namely the Zenne, Dijle and Scheldt-Belgium rivers [36]. Based on [15], the processes that are involved in the mineralization of fluvial organic matter are mainly anaerobic, with are also associated with sulfate oxidation. During sulfate oxidation,  $\text{HCO}_3^-$  is primarily formed and,  $\text{CO}_{2(\text{aq})}$  can be produced via methanogenesis after the reoxidation of these compounds.

The DIC concentrations in the Capibaribe River (mean =  $1043 \mu\text{mol}\cdot\text{kg}^{-1}$ ) were higher than those reported by [7] for tropical rivers ( $645 \mu\text{mol}\cdot\text{kg}^{-1}$ ). According to this

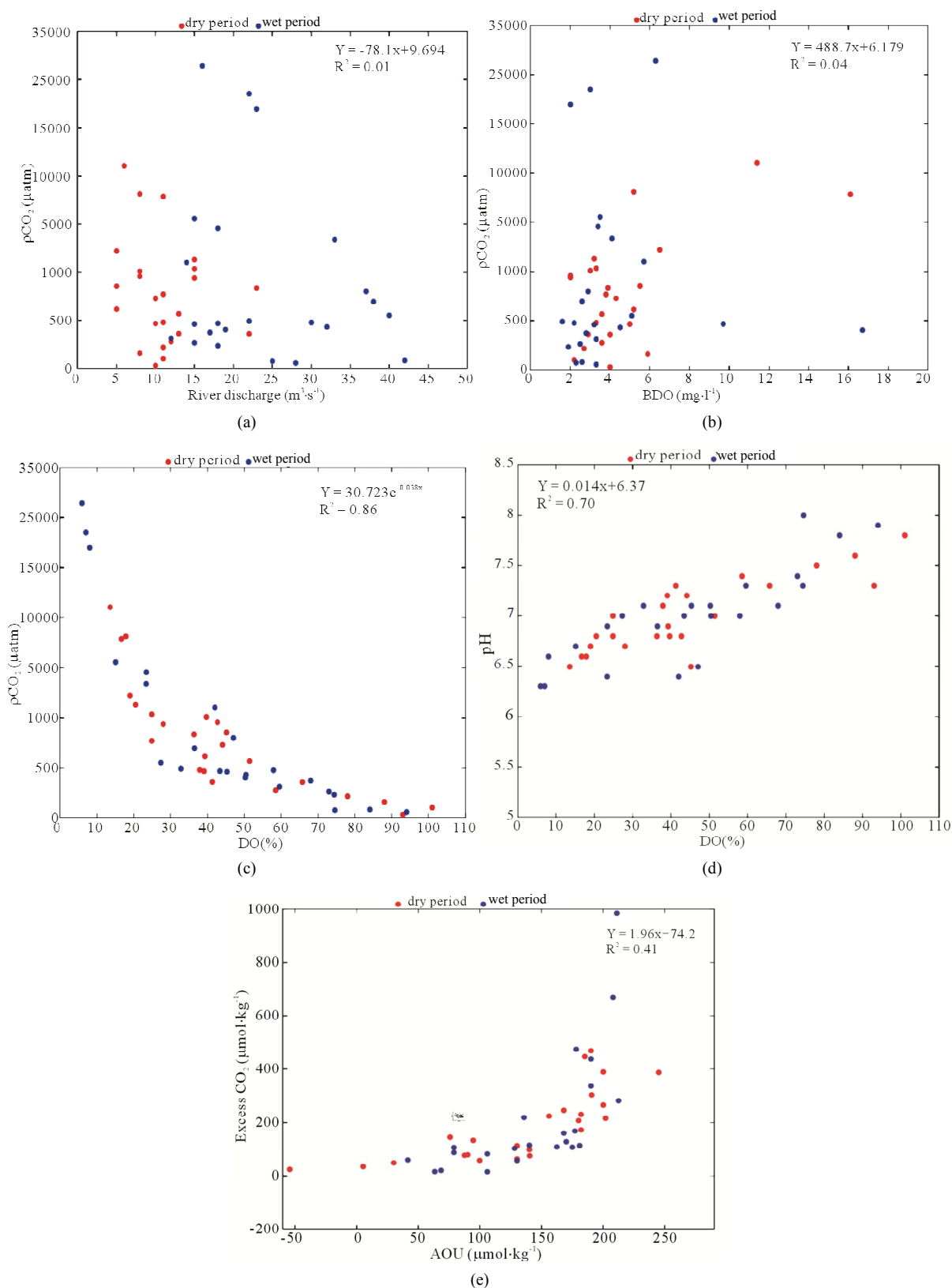
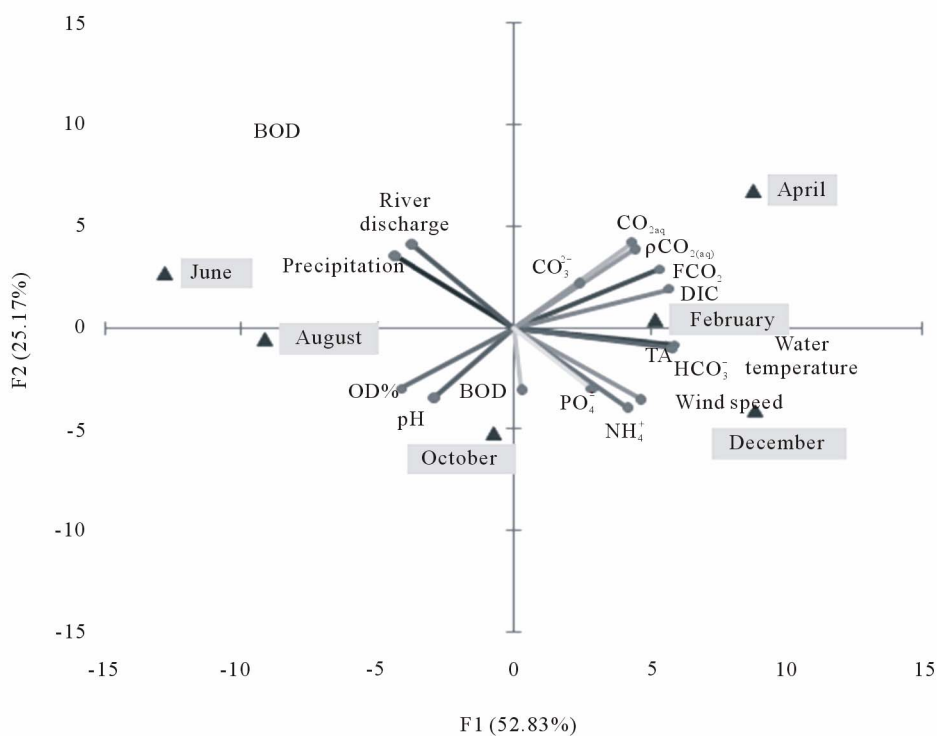


Figure 6. Correlations between the river- and carbonate system-linked variables in the 2002-2010 data series in the Capi-baribe River (CB-72/CPRH). (a)  $p\text{CO}_2$  vs. fluvial discharge; (b)  $p\text{CO}_2$  vs. BOD; (c)  $p\text{CO}_2$  vs. DO%; (d) pH vs. DO% and (e)  $\text{CO}_2$  excess vs. AOU.

**Table 2. Factor loadings of principal component analysis performed with the variables analyzed for the Capibaribe River, Brazil, during 2002-2010.**

Variable	Factor load				
	F1	F2	F3	F4	F5
pH	-0.813	0.500	-0.100	0.132	0.080
Salinity	0.035	0.755	-0.463	-0.119	0.086
Water temperature	0.291	0.604	0.280	-0.390	0.231
Wind speed	0.123	0.316	0.671	-0.200	-0.080
PO <sub>4</sub> <sup>-</sup>	0.495	0.099	0.226	0.202	0.655
TA	0.380	0.841	-0.276	0.098	-0.032
Precipitation	-0.385	-0.575	-0.588	-0.149	0.247
River discharge	-0.374	-0.555	-0.600	-0.232	0.266
DIC	0.834	0.372	-0.352	0.055	-0.104
HCO <sub>3</sub> <sup>-</sup>	0.405	0.828	-0.266	0.097	-0.038
CO <sub>3</sub> <sup>2-</sup>	-0.511	0.569	-0.375	0.036	0.150
FCO <sub>2</sub>	0.910	-0.066	-0.151	-0.023	-0.038
BOD	0.394	-0.063	0.187	0.572	0.525
OD%	-0.822	0.318	0.014	0.160	0.011
AOU	0.742	-0.433	-0.030	-0.006	0.123
pCO <sub>2(air)</sub>	0.032	-0.196	-0.158	0.881	-0.307
pCO <sub>2(aq)</sub>	0.891	-0.169	-0.173	-0.180	-0.055
CO <sub>2aq. excess</sub>	0.886	-0.183	-0.249	-0.040	-0.145
NH <sub>4</sub> <sup>+</sup>	0.456	0.253	0.312	0.283	0.530

**Figure 7. Principal component analysis of the variables that were investigated in the 2002-2010 period in the Capibaribe River, Brazil.**

author, the dissolved organic carbon (DOC) concentrations for tropical rivers vary around  $448 \mu\text{mol}\cdot\text{kg}^{-1}$  and are directly associated with the organic discharges from domestic and industrial sources [42]. Following the equation proposed by [4] ( $\text{DOC} = 0.65 \times \text{HCO}_3^-$ ), a DOC concentration of  $550 \mu\text{mol}\cdot\text{kg}^{-1}$  was determined for the Capibaribe River. This value is 1.2 times the global mean for tropical rivers estimated by [7] and thus reinforces the high concentrations of carbonate system compounds that are associated with anthropogenic actions.

The principal component analysis (PCA) performed with the set of studied variables is shown in **Figure 7** and detailed in **Table 2**. The PCA showed an association between the months of April, February and December with  $p\text{CO}_{2(\text{aq})}$ ,  $\text{FCO}_2$  and the variables associated with the carbonate system ( $\text{DIC}$ ,  $\text{TA}$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{CO}_{2(\text{aq})}$ ). Precipitation in the basin and the fluvial discharge in the Capibaribe River were associated with June, while the  $\text{DO}\%$  was associated with August. The wind intensity and water temperature were both associated with December.

During the dry months (December and February), the mean water temperature was  $1.5^\circ\text{C}$  higher when compared with the mean for the months of the wet period. During the dry period, biological activity, which is critical for the production and consumption of  $\text{CO}_{2(\text{aq})}$  in the rivers, is strongly influenced by physical factors such as temperature, light and fluvial discharge, and this activity can vary on a scale of minutes, days or seasonally [35]. Although daily variations in pH and  $\text{CO}_{2(\text{aq})}$  as a result of photosynthesis and respiration are expected to have a stronger effect during the dry period, the results always showed positive  $\text{FCO}_2$  throughout the time series, indicating that the body of water is producing gas.

The mean  $p\text{CO}_2$  value found for the Capibaribe River ( $8340 \mu\text{atm}$ ) was lower than that observed by [15] in the Tietê River, Brazil ( $11,109 \mu\text{atm}$ ) and higher than that observed by [41] in the Piracicaba River, Brazil ( $5,974 \mu\text{atm}$ ). The mean  $p\text{CO}_2$  values in three tropical African rivers ranged from 1925 to  $9595 \mu\text{atm}$  [43]. Studies conducted on other non-tropical but equally polluted rivers showed similar values to those observed in the Capibaribe River. The Dijle, Dender and Scheldt rivers, located in Belgium and the Netherlands, for example, showed mean  $p\text{CO}_{2(\text{aq})}$  values of 7252, 8300 and  $9500 \mu\text{atm}$ , respectively [36].

The results of the  $\text{FCO}_2$  calculations during 2002-2010 show a high and continuous release of gas to the atmosphere (mean =  $+225 \text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ), indicating that the Capibaribe River maintains itself in a heterotrophic manner throughout the time period. These values agree with the estimates obtained for other rivers worldwide, regardless of whether they are highly impacted by anthropogenic actions. For example, African hydrographic

basins with population densities below 100 inhabitants  $\text{km}^{-2}$  exhibit a mean value of  $+119 \text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$  [43], which is half of the mean value observed in the Capibaribe River. One study [44] estimated that the Amazonian rivers are characterized by a mean flux of  $+830 \text{g}\cdot\text{C}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$  ( $+51.6 \text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ), while another study [45] estimated a mean flux of  $2370 \text{g}\cdot\text{C}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$  ( $147.5 \text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ) for the rivers of the United States.

The findings of the present study of the Capibaribe River confirm the significance of densely urbanized coastal tropical systems in terms of their input of nutrients and  $\text{CO}_2$  to the adjacent estuaries and coastal regions, reinforcing the need of continuous and long-term measurements to enable the accurate quantification of the  $\text{CO}_2$  input to the atmosphere.

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