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Carbon dioxide emissions from estuaries of northern and northeastern Brazil

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The carbon dioxide flux through the air–water interface of coastal estuarine systems must be quantified to understand the regional balance of carbon and its transport through adjacent coastal regions. We estimated and calculated the emissions of carbon dioxide (FCO_2) and the partial pressure of CO_2 (pCO_2) values in 28 estuarine environments at a variety of spatial scales in the northern and northeastern regions of Brazil. The results showed a mean FCO_2 (water to air) of 55 ± 45 mmol·m^{-2}·d^{-1}. Additionally, a negative correlation between dissolved oxygen saturation and pCO_2 was observed, indicating a control by biological processes and especially by organic matter degradation. This leads to increased dissolved CO_2 concentration in estuarine waters which results in a pCO_2 that reached 8,638 µatm. Our study suggests that northern and northeastern Brazilian estuaries act as sources of atmospheric CO_2. The range of pCO_2 observed were similar to those found in inner estuaries in other places around the world, with the exception of a few semi-arid estuaries (Köppen climate classification – *BSh*) in which record low levels of pCO_2 have been detected.

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 sources of CO_2 to the atmosphere[1–4]. Estuaries are often strongly influenced by human activities. Attention has been focused on estuaries as potentially important sites of organic matter cycling in the coastal zones in recent decades. Estuaries are regarded as sources of CO_2 to the atmosphere because of their elevated loads of detrital organic matter that drives intense respiration[5].

The exchange of CO_2 between inner estuaries and the atmosphere has been recently evaluated using data from 106 systems[6]. The estimated global emissions of 0.26 Pg C year^{-1} from these systems is lower than previous estimates, which have been in the range of 0.27 to 0.60 Pg C year$^{-11,2,7-9}$. However, all recent studies have reported higher values than those first reported (0.1 Pg C year^{-1})[10].

Very little is known about the seasonal and interannual variability of the CO_2 flux at the air–water interface in rivers and estuaries of Brazil, and particularly in the northeastern region of the country. Recently, two studies in tropical estuaries in northeastern Brazil reported values of 30 and 35.6 mmol m^{-2} d$^{-111,12}$.

The climatic diversity found in the basins of the Atlantic coast of Brazil is a function of their position in relation to atmospheric circulation systems such as the South Atlantic tropical cyclone and the polar anticyclone. The basins of the Atlantic coast present a range of climates from the warm tropical climate of the south to humid and semi-humid climates as well as semi-arid regions in the north[13].

To quantify CO_2 emissions from the Brazilian estuaries, water samples were collected monthly from 6 estuaries (12 months - 72 observations). Additionally, we estimated the amount of carbon emissions from rivers and estuaries using measurements of salinity, temperature, alkalinity and pH at low tide from 22 systems (78 observations) along the northern and northeastern Brazilian coast during the wet and dry periods (Fig. 1).

The objectives of this study are to characterize and quantify the variability of CO_2 emissions and the variables associated with the carbonate system in the tropical systems located in northern and northeastern Brazil. The characterization of these emissions is associated with population density, climate type and estuarine gradient. Finally, we assess the contribution of excess CO_2 input by rivers to the total CO_2 emission to the atmosphere from the estuaries through correlation with others species of the carbonate system, as well as oxygen and nutrients.

Results

Climatology and fluvial discharge. The mean annual water discharge from the Brazilian estuaries studied here varies from 1.0 to 5,946 m^3 s^{-1}, contributing with 8,740 m^3 s^{-1} (276 km^3 year^{-1}) to the Atlantic Ocean (Table 1). The observed pluviometric precipitation and evaporation were not significantly different from their historical averages (1982–2012) (t-test; $\alpha = 0.05$). The relationship between river discharge and pCO_2 was explored for each
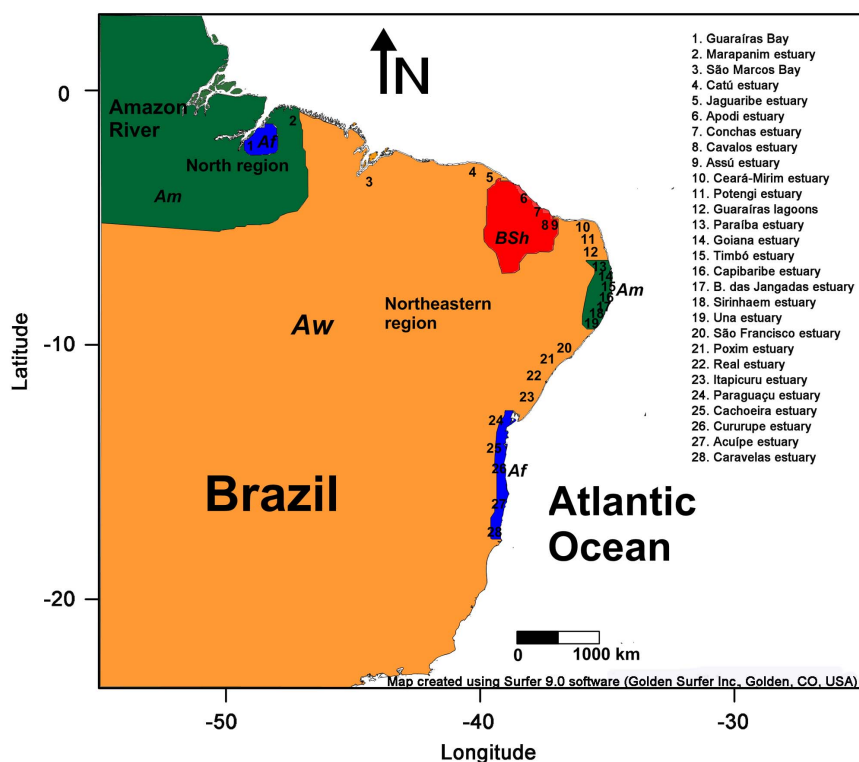
Figure 1 | The Köppen climate classification[29] of the Brazilian estuaries considered in this study: *Am* (tropical wet climate), *Af* (tropical rainforest climate), *Aw* (tropical wet and dry or savanna climate) and *BSh* (semi-arid climate). Map generated with Surfer 9.0® software.

system (18 systems; Table 2). The river discharge was positively correlated with pCO_2 values in 44.4% of the systems. However, the systems that showed a positive correlation in Table 2 showed no association with population density or a specific climate type.

Distribution of physical and chemical parameters. The salinity varied widely along the coast (0.2–46 units), indicating a strong interaction with precipitation and evaporation as well as soil characteristics of the drainage basins (Table 1). Low salinities were found in the upper estuaries and in Guajará Bay (in the northern region). High salinities (38.8–46 units) were observed in the latitudinal band between −4.8° and −5.1° (the Apodi, Conchas, Cavalos and Assu Estuaries). The water balance was negative in these estuaries because evaporation was 8.5 fold higher than precipitation. The Spearman correlation coefficient values indicated that salinity was positively correlated ($\alpha = 0.05$) with temperature, TA, DO% and pH and negatively correlated with pCO_2 and CO_2 fluxes (FCO_2).

Water temperatures along the coast ranged from 24.6 to 29.5°C. The estuaries of the northern region (Guajará Bay, Marapanim and São Marcos Bay) had temperatures that were 3.6°C higher (averages: 28.9–25.3°C) than the estuaries located at the other extreme of the latitudinal band (Cururupe, Acuípe and Caravelas).

The pH values in the monitored estuaries varied widely (from 6.60 to 8.20) (Table S1; Supplementary Material). Low values (<7.0) were observed in the northern (Guajará Bay) and southern (the Real, Cururupe and Acuípe Estuaries) regions, whereas high values (>7.8) were observed in the northeastern estuaries (Catu, Jaguaribe, Apodi, Conchas and Cavalos) located between latitude −3.9° and −5.1°. The correlation between pH values and DO% values was low ($r^2 = 0.49$; $p < 0.0001$) (Fig. 2a).

The estuarine systems had a mean Dissolved Oxygen (DO) saturation of $67 \pm 18\%$ and a mean DO concentration of 146 ± 60 µmol L^{-1} (Table S1; Supplementary Material). Values lower than 156 µmol L^{-1} are below the limit recommended in the Brazilian

legislation[14]. In this study, 50% of the samples tested had DO concentrations below this limit (156 µmol L^{-1}). A regression analysis demonstrated a strong negative exponential correlation between DO% and pCO_2 ($r^2 = 0.92$; $p < 0.0001$) (Fig. 2b).

TA and DIC in the Brazilian monitored estuaries (Table 1 and Supplementary Material S1) varied widely between 131 and 2,800 µM for TA and between 241 and 2,527 µM for DIC. High DIC concentrations (>2,000 µM) were observed in the northeastern estuaries (Apodi, Conchas, Cavalos, Assu, Potengi and Caravelas), whereas lower values (<400 µM) were observed in the northern and southern estuaries (Guajará Bay and Cururupe). TA and DIC were strongly correlated with salinity and pH (Spearman's correlation; $r = 0.7$; $\alpha = 0.05$; $p < 0.0001$).

pCO_2 and CO_2 emissions (FCO_2). The pCO_2 values (Table 1) varied widely between 162 and 8,638 µatm in northern and northeastern estuaries. The pCO_2 values of estuaries that receive low water discharges (<50 m³s^{-1}) were not significantly different from those of estuaries that receive high water discharges (>50 m³s^{-1}) ($\alpha = 0.05$; $p < 0.7$). A Spearman correlation analysis showed a strong negative correlation ($\alpha = 0.05$) between pCO_2 and salinity, DO% and pH. The pCO_2 in the water was significantly different in the dry and rainy seasons ($\alpha = 0.05$; $p < 0.01$). Monthly mean pCO_2 in the rainy season was 1.5-fold higher than in the dry season. According to the results of Kruskal–Wallis tests ($\alpha = 0.05$; $p < 0.001$), the estuaries laying in different climate types (*Af*, *Am*, *Aw* and *BSh*) had significantly different pCO_2 values. pCO_2 values were 2 to 3.3-fold higher in estuarine systems located in the *Af*, *Am* and *Aw* climate zones than those of the system located in the *BSh* climate zone (Fig. 3). The Kruskal–Wallis test also revealed significant differences ($\alpha = 0.05$; $p < 0.01$) in the pCO_2 values of the different estuary types (tidal fresh/upper, inner, middle and lower estuaries). The pCO_2 values in the lower systems were 1.5–2.6-fold lower than those in the tidal fresh/upper, inner and middle estuaries (Fig. 3).

Table 1 | Drainage area, population density (inhabitants/km²) and mean values of river discharge (annual average), salinity, temperature, total alkalinity, pCO_2 and CO_2 fluxes in northern and northeastern estuaries in Brazil

Number	System	Area (km²)	River Discharge (m³s⁻¹)	Pop. Dens.	Number of Samples	Tidal Amplitude (m)	Salinity Mean (range)	T (°C) Mean (range)	TA (μmol L⁻¹) Mean (range)	pCO_2 (μatm) Mean (range)	Flux (mmol CO_2 m⁻² d⁻¹) Mean (range)	Estuarine Division
1	Guajará Bay	750	5,946	1,000	4	3.5	0.3 (0.1–0.6)	28.5 (28–29)	131 (107–145)	3,520 (984–6,145)	+85.7 (+22–+159)	Tf/upper
2	Marapanim	120	95	35	3	5.6	16.8 (10–29)	29.3 (29–30)	1,746 (1,720–1,760)	3,240 (690–8,260)	+126.7 (+28.8–+324)	Inner
3	São Marcos Bay	2,000	316	174	2	6.4	19.7 (16.8–22.6)	28.9 (27.8–30)	730 (750.4–708.6)	560 (459–661)	+4.80 (+2.1–+7.5)	Middle
4	Catú	1.3	1.5	130	8	3.0	7.2 (2.8–19)	28.7 (25.8–32)	1,247 (595–2,804)	430 (252–672)	+2.45 (−7–+11.6)	Inner
5	Jaguaribe	64	57	40	3	3.0	26.3 (22.7–29.6)	29.0 (28.3–29.4)	1,711 (967–2,787)	753 (432–1,292)	+18.0 (+4.4–+45)	Lower
6	Apodi	11	6.1	23	1	2.8	44.0	28.6	2,760	385	+0.9	Lower
7	Conchas	2.4	3	16	1	2.8	38.8	28.2	2,790	897	+42.6	Lower
8	Cavalos	4.1	3.4	32	1	2.8	42.8	29.5	2,800	996	+50	Lower
9	Assu	5.6	4.5	62	1	2.8	46.0	28.2	2,550	400	+2.3	Lower
10	Ceará-Mirim	2.5	2.7	59	1	2.7	3.5	28.8	1,600	3,639	+164.7	Lower
11	Potengi	14.1	3	440	1	2.7	23.8	29.3	2,210	1,738	+77.3	Middle
12	Guaraíras lagoons	21.6	7.5	180	1	2.7	10.7	28.2	1,710	1,682	+78.3	Inner
13	Paraíba	70	152	298	2	2.6	21.0 (13.2–28.7)	28.0 (28–28)	1,127 (1,031–1,223)	3,052 (864–5,240)	+119.5 (+21.2–+217.8)	Middle
14	Goiana	20	20	151.4	12	2.3	16.0 (1.8–34.5)	27.0 (25.1–29.1)	977 (400–1,663)	928 (204.4–1,898)	+36.1 (−6–+142)	Inner
15	Timbó	14.6	15	724	12	2.3	16.7 (5–32.2)	27.0 (25.3–29.9)	1,077 (510–1,674)	1,264 (166–2,437)	+55.3 (+2.5–+124.6)	Inner
16	Capibaribe	35	25	1,000	12	2.3	13.6 (3.1–32.4)	27.6 (25.9–30.5)	982 (502–1,301)	1,555 (617–3,291)	+43.0 (+7.8–+115.4)	Inner
17	Barra das Jangadas	13	15	1,460	12	2.3	13.0 (4–24.3)	27.3 (25.6–30.1)	942 (402–1,483)	1,324 (388–2,511)	+54.0 (+1.1–+141.5)	Inner
18	Sirinhaem	10	34.7	110	12	2.3	17.3 (4–33)	27 (25.6–30.5)	897 (450–13,51)	823 (162–1,415)	+16.4 (−9.1–+37.5)	Inner
19	Una	11	45	175	12	2.3	10.7 (0.6–33.2)	27.0 (24.3–28.8)	715 (339–1,400)	965 (385–1,979)	+25.7 (+0.4–+100.2)	Inner
20	São Francisco	800	1,858	22	12	2.2	4.6 (3.1–6.7)	26.8 (25.2–29)	745 (517.2–1,044)	468 (363–547)	+6.3 (−1.2–+11.7)	Tf/upper
21	Poxim	4	1	255	4	2.2	11.8 (1.4–22.6)	26.1 (22.3–29)	1,075 (816–1,708)	1,522 (250–3,470)	+48.7 (−8.0–+118.4)	Inner
22	Real	12	10	30	4	2.2	0.2 (0.1–0.5)	26.4 (24.8–28.3)	377 (171–882)	3,564 (1,573–7,152)	+81.6 (+33.7–+160)	Tf/upper
23	Itapicuru	15	20	23	4	2.2	0.8 (0.4–1.2)	28.3 (25.7–30.3)	726 (525–997)	2,318 (614–6,221)	+55.0 (+10.5–+160)	Tf/upper
24	Paraguaçú	128	64.3	166	7	2.7	0.2 (0.1–0.3)	27.2 (26.6–28.5)	467 (359–779)	2,025 (313–6,464)	+49.6 (−1.4–+201.6)	Tf/upper
25	Cachoeira	16	22	138	4	2.2	12.0 (0.5–23.6)	29.3 (25.7–31.6)	1,598 (629–2,225)	1,051 (407–1,517)	+20.5 (+1.6–+33.7)	Inner
26	Cururupe	3.9	2	8	6	2.2	1.4 (0.6–3.7)	24.8 (23.7–26.2)	281 (105–600)	2,250 (221–3,288)	+61.4 (−6.2–+108)	Tf/upper
27	Acuípe	9	4	5	6	2.2	2.0 (0.6–3.2)	24.6 (23.5–26)	293 (100–575)	3,426 (649–8,638)	+175.2 (+10–+498)	Tf/upper
28	Caravelas	63.4	5	100	2	2.2	33.5 (33.1–34)	26.7 (25–28.4)	2,375 (2,130–2,620)	1,051 (722–1,380)	+23.3 (+10.5–+36)	Lower
	Total	4,221.5			150							

Table 2 | Mean values of river discharge (Q), sample number (n), salinity, equations of fit of the pCO_2 as a function of Q, r^2 ($p > F$) and pCO_2 values. The best goodness of fit is shown in bold (r^2)

| System	Q (m³ s⁻¹) Mean (range)	n	Salinity Mean (range)	Equation Formulation	r^2	pCO_2 (µatm) Mean (range)
Guajará Bay	5,946 (5,640–6,100)	4	0.3 (0.1–0.6)	$pCO_2 = -53{,}057 + 9.5 \times Q$	**0.60** ($p < 0.1$)	3,520 (984–6,145)
Marapanim	95 (65–130)	3	16.8 (10–29)	$pCO_2 = 13{,}296 - 106 \times Q$	**0.64** ($p < 0.4$)	3,240 (690–8,260)
Catú	1.5 (0.4–4.0)	8	7.2 (2.8–19)	$pCO_2 = 322.3 + 72 \times Q$	0.37 ($p < 0.1$)	430 (252–672)
Jaguaribe	57 (22–90)	3	26.3 (22.7–29.6)	$pCO_2 = 52.7 + 12.2 \times Q$	**0.78** ($p < 0.3$)	753 (432–1,292)
Goiana	20 (10–40)	12	16.0 (1.8–34.5)	$pCO_2 = 428.4 + 25.5 \times Q$	0.20 ($p < 0.1$)	928 (204.4–1,898)
Timbó	15 (6.0–28)	12	16.7 (5–32.2)	$pCO_2 = 464 + 55.2 \times Q$	**0.50** ($p < 0.1$)	1,264 (166–2,437)
Capibaribe	25 (10–40)	12	13.6 (3.1–32.4)	$pCO_2 = 1{,}010 + 22.3 \times Q$	0.30 ($p < 0.3$)	1,555 (617–3,291)
Barra das Jangadas	15 (6.0–28)	12	13.0 (4–24.3)	$pCO_2 = 1{,}316 + 0.61 \times Q$	0.10 ($p < 0.9$)	1,324 (388–2,511)
Sirinhaem	34.7 (17–55)	12	17.3 (4–33)	$pCO_2 = 635 + 5.4 \times Q$	0.20 ($p < 0.6$)	823 (162–1,415)
Una	45 (30–65)	12	10.7 (0.6–33.2)	$pCO_2 = -94.5 + 23.6 \times Q$	**0.51** ($p < 0.01$)	965 (385–1,979)
São Francisco	1,858 (1,700–2,010)	12	4.6 (3.1–6.7)	$pCO_2 = 421.3 + 2.5 \times Q$	0.04 ($p < 0.9$)	468 (363–547)
Poxim	1 (0.5–2.0)	4	11.8 (1.4–22.6)	$pCO_2 = -529.2 + 2{,}002 \times Q$	**0.93** ($p < 0.02$)	1,522 (250–3,470)
Real	10 (5.7–16)	4	0.2 (0.1–0.5)	$pCO_2 = 1{,}948 + 163 \times Q$	0.30 ($p < 0.6$)	3,564 (1,573–7,152)
Itapicuru	20 (15–31)	4	0.8 (0.4–1.2)	$pCO_2 = 4{,}516 - 108.5 \times Q$	0.10 ($p < 0.7$)	2,318 (614–6,221)
Paraguaçú	64.3 (22–130)	7	0.2 (0.1–0.3)	$pCO_2 = 3{,}543 - 23.6 \times Q$	0.20 ($p < 0.3$)	2,025 (313–6,464)
Cachoeira	22 (13–35)	4	12.0 (0.5–23.6)	$pCO_2 = 69 + 44.6 \times Q$	**0.81** ($p < 0.1$)	1,051 (407–1,517)
Cururupe	2 (1.0–3.4)	6	1.4 (0.6–3.7)	$pCO_2 = 406.7 + 906.5 \times Q$	**0.50** ($p < 0.1$)	2,250 (221–3,288)
Acuípe	4 (2.0–7.0)	6	2.0 (0.6–3.2)	$pCO_2 = 400 + 750.3 \times Q$	0.30 ($p < 0.3$)	3,426 (649–8,638)
Total		137				

The FCO_2 of the monitored Brazilian estuaries ranged between 0.9 and 175.2 mmol m⁻² d⁻¹ (Table 1; Fig. 4) with a mean rate of 55 ± 45 mmol m⁻² d⁻¹. CO_2 emissions significantly differed ($\alpha = 0.05$; $p < 0.01$) seasonally, with monthly rates 1.8-fold higher during the rainy season when compared with the dry season (Fig. S1; Supplementary Material). The Kruskal–Wallis tests ($\alpha = 0.05$; $p < 0.01$) for the climate types (*Af*, *Am*, *Aw* and *BSh*) demonstrated significant differences in the CO_2 fluxes. CO_2 emissions in the estuaries characterized by *Af*, *Am* and *Aw* climates were 2.2–2.8-fold higher than those in the system within the *BSh* climate (Fig. 3). The Kruskal–Wallis test also demonstrated significant differences in CO_2 emissions ($\alpha = 0.05$; $p < 0.001$) according to estuarine type (inner, middle or lower), where the lower systems showed 2–3.6-fold lower rates (Fig. 3).

CO_2 emissions from 4,222 km² of estuarine area in the northern Brazilian were estimated to be 1.01 Tg C y⁻¹.

Discussion

The processes that partition dissolved CO_2, pCO_2 and DIC in estuarine environments are complex and are influenced by a combination of factors and natural processes, such as the types of rock and soil in the hydrographic basin, the water–atmosphere interactions and the oxidation/reduction reactions of anthropogenic inputs[4]. However, most of these processes are controlled primarily by the pH. The results of this study indicate that the typical tropical coastal systems in the northern and northeastern regions of Brazil reflect significant heterotrophy in terms of the CO_2 fluxes (average: 55 ± 45 mmol m⁻² d⁻¹) and the high levels of pCO_2 observed (average: 1,564 µatm). Analyses were conducted to determine whether the rock and soil types influence the water CO_2 content. No correlation between fluvial discharge and pCO_2 was observed, suggesting that the transport processes via fluvial runoff are not the primary factors responsible for the high concentrations of dissolved CO_2 found in the Brazilian estuaries monitored in this study. Other studies have shown that the lack of correlation between these two variables is characteristic of basins that are located in populous industrialized areas[15]. For example, in the Zenne River (an urban river in Brussels, Belgium), periods of high fluvial discharge have not been found to be correlated with high pCO_2 values[16]. PCA analysis results (Fig. 5) showed a strong positive correlation between rainfall and pCO_2 in Guajará Bay (in the northern region). Guajará Bay had the highest river discharge of the systems studied (5,946 m³ s⁻¹) as a result of the high runoff of the Pará River. In the northern region (systems 1 to 3; Fig. 1 and Fig. 3), tropical climate (*Af* and *Am* types) predominates precipitation in this region is 2.3-fold higher than in the northeastern region (systems 4 to 28; Fig. 4). However, the evaporation in the northeastern region is 2-fold higher than that in the northern region. The *BSh* climate (4 systems) strongly influenced this result. The climate in this region is semi-arid (*BSh* type), and the estuaries are surrounded by shrimp farms, salt ponds and agricultural areas. The mean annual freshwater discharge in the region was 4.3 m³s⁻¹, and the rate of evaporation was 8.5-fold higher than the precipitation measured during this study. The difference between the mean temperatures of the northern and northeastern regions was 1.3°C. The reported mean temperatures of the water masses adjacent to the coasts of the northern and northeastern regions of Brazil were 27.6°C and 27.2°C[17,18], respectively. We obtained similar results for the estuaries of the northern and northeastern regions (28.5°C–27.6°C; Table 1).

A strong negative correlation between DO% and pCO_2 (Fig. 2b) was detected, suggesting that intense organic matter decomposition in the estuaries, either in the water column or the sediment, results in a decrease in pH (Fig. 2a) and enhanced pCO_2 values. Other processes such as direct groundwater discharge, biogeochemical reactivity at seepage faces or benthic organic matter processing could also influence the observed surface water composition in these estu-
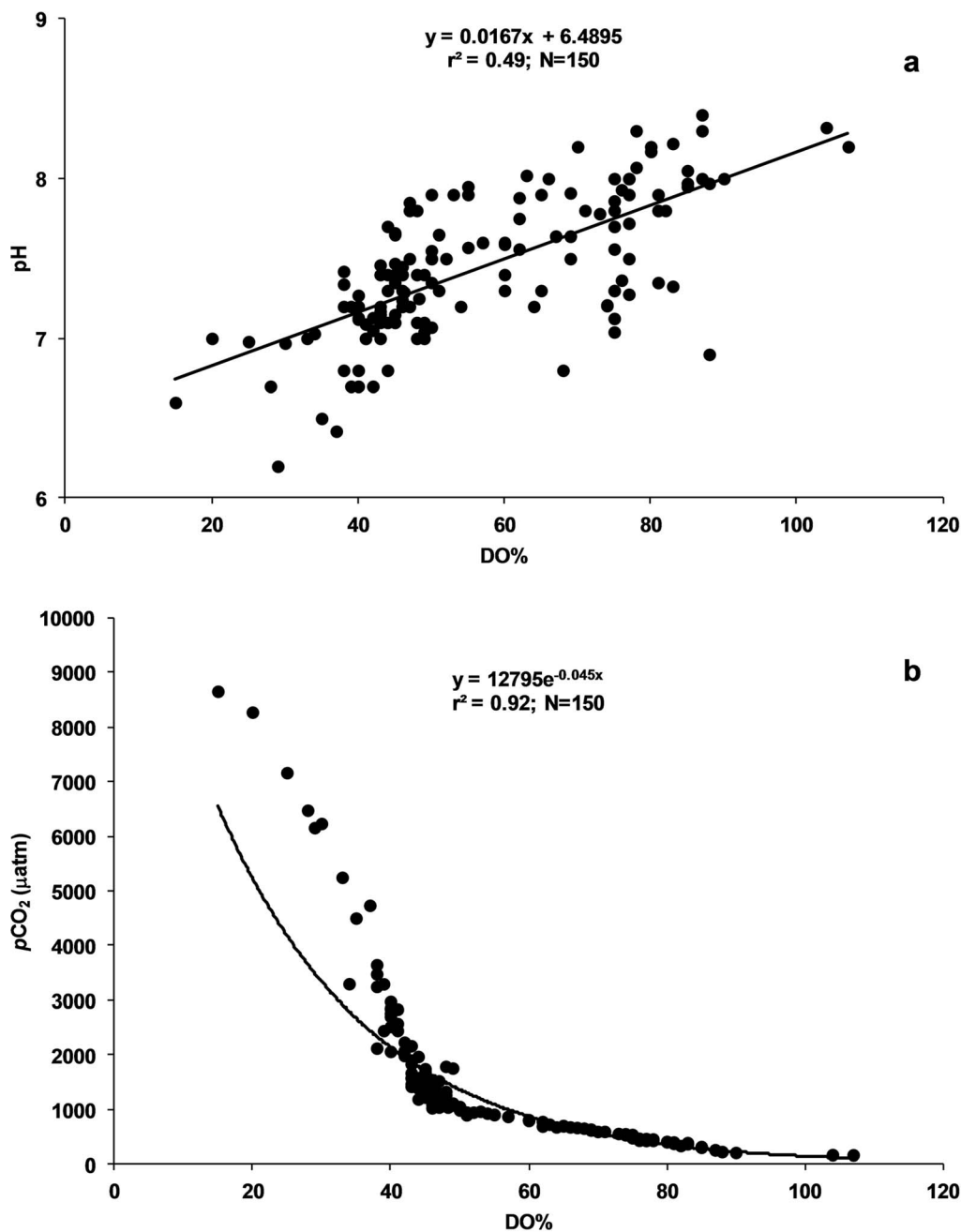
Figure 2 | **The relationship between DO (%) and pH (a) and pCO$_2$ (b).**

aries[19–21]. Additionally, the AOU (Table S1; Supplementary Material) was positively correlated with the excess CO$_2$ ($r^2 = 0.51$; $p < 0.0001$), which indicates that the organic load that enters the systems has a significant impact on the microbial processes that are associated with the carbon and nitrogen cycles. The DIP measurements were strongly correlated with pCO$_2$ values in systems where the population density was >100 inhabitants/km^2 ($r^2 = 0.51$; $p < 0.002$). This nutrient enrichment can lead to the excessive production of algal biomass and consequently to eutrophication. Under high CO$_{2(aq)}$ values, which result from bacterial respiration, carbonic acid is produced and the water pH decreases[15]. If the characteristics of a water body are such that the CO$_2$ concentration in the aqueous media is close to equilibrium with the atmospheric CO$_2$ levels, strong correlation among TA, pCO$_2$ and pH can be expected. However, the complex set of processes that lead to the production or consumption of CO$_{2(aq)}$ and the production or removal of carbonic acid (HCO$_3^-$) prevent the establishment of a correlation among TA, pH and

pCO$_2$[4,15]. TA exhibited a strong correlation with pH but not with pCO$_2$. High TA values (average: 1,298 μmol L^{-1}) may therefore be associated with the high values of HCO$_3^-$ that are found mainly in the northeastern systems, which represent 90% of the total DIC; CO$_3^{2-}$ represents 6% of the total DIC, and the remaining 4% is associated with CO$_{2(aq)}$. These values are consistent with those recorded for highly polluted systems, including tropical rivers, such as the Capibaribe and Tietê Rivers in Brazil[4,22], and temperate systems, namely, the Scheldt estuary and its tributaries Zenne and Dijle (Belgium and the Netherlands)[16].

DIC concentrations in the Brazilian estuaries (average: 1,229 μmol L^{-1}) were higher than those reported for tropical rivers (average: 695 μmol L^{-1})[23] and lower than those reported for Indian estuaries (average: 1,777 μmol L^{-1})[24].

In the inner and upper estuaries, the impoverishment in oxygen due to organic matter remineralization is accompanied by an increase in DIC, TA and pCO$_2$ and a decrease in pH. TA concentra-
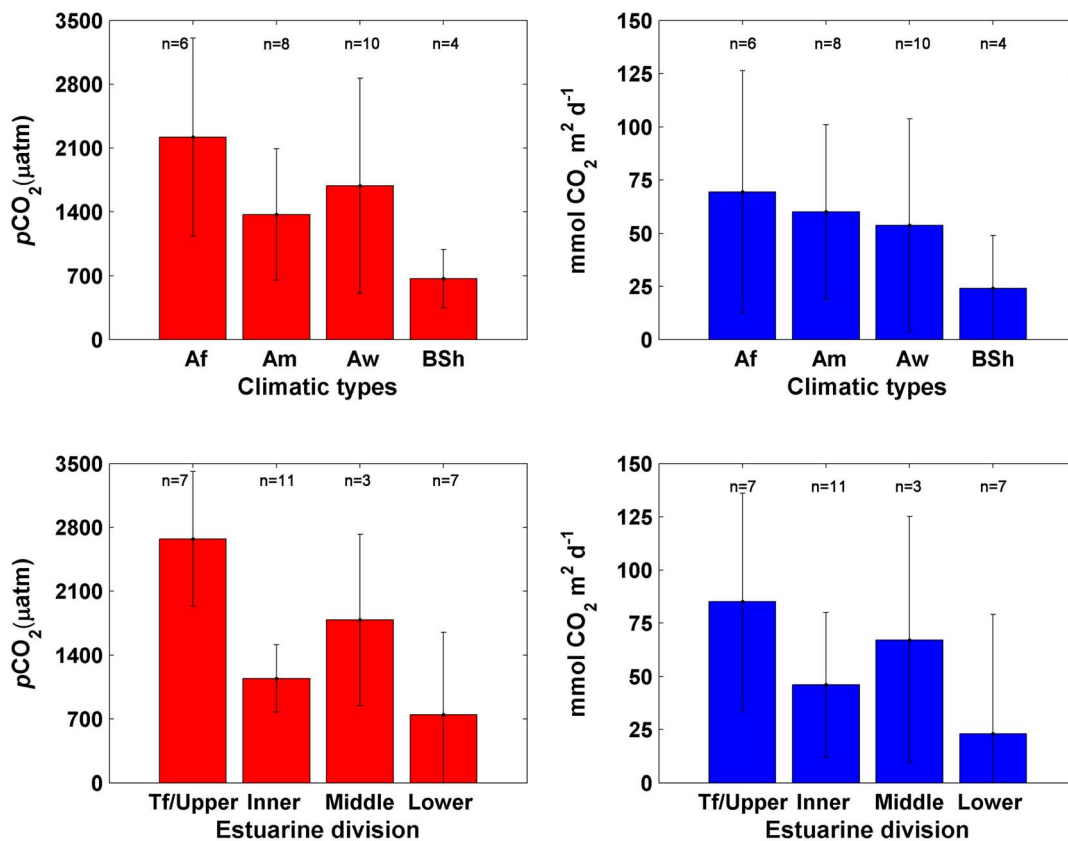
Figure 3 | pCO_2 and FCO_2 (averages values) according to climatic type and estuary type for the northeastern Brazilian estuaries. n indicates the number of samples.
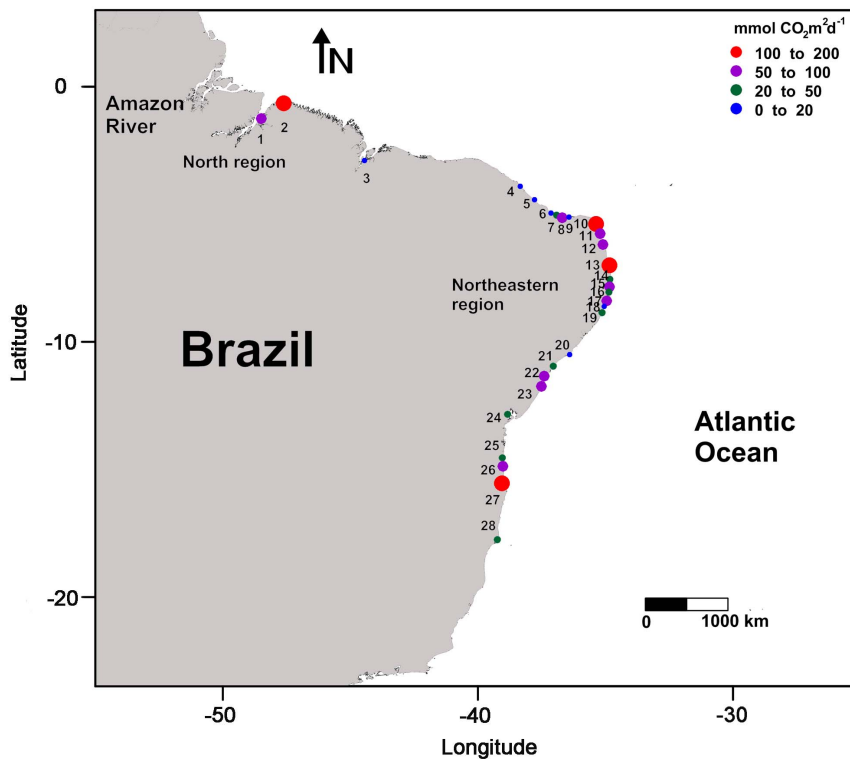

Figure 4 | FCO_2 levels of the northeastern Brazilian estuaries. The numbers represent the estuaries shown in Fig. 1 (figure generated with Surfer 9.0 ® software).

tions may have also been affected by the incorporation of fulvic and humic acids originated from the mangrove areas or urban sewage[11], contributing to the high values of TA as noted above.

The average pCO_2 in the Brazilian estuaries varied widely, reaching levels up to 8,638 µatm. The pCO_2 levels observed in the Brazilian estuaries are within the reported range for other estuaries around the world. A recent study estimated that on average, upper estuaries around the world have a pCO_2 of 3,033 ± 1,078 µatm[6]. This value is similar to that observed in the present study (average: 2,674 µatm) for the tidal fresh and upper estuaries (Fig. 3). Our pCO_2 values for the middle and lower estuaries (average: 1,783 and 747 µatm, respectively) were also similar to those reported for other estuaries around the world (2,277 ± 626 and 692 ± 178 µatm, respectively)[6] (Fig. 3). Similar values to those presented here were reported by recent studies for tropical estuaries in the northeastern region of Brazil (4,700 ± 2,420 and 2,200 ± 360 µatm, respectively)[11,12]. The pCO_2 supersaturation found in the upper estuaries is not unusual, as estuaries are generally highly heterotrophic ecosystems where the organic carbon carried by rivers is partially remineralized. The spatial pCO_2 patterns of the Brazilian estuaries exhibited trends similar to those observed for other estuaries around the world.

The average FCO_2 from the Brazilian estuaries is 54.4 ± 45 mmol CO_2 m^{-2} d^{-1}. This value is 2-fold higher than that reported for Indian estuaries (27 mmol CO_2 m^{-2} d^{-1})[24] and 0.73-fold higher than that presented for tidal systems and small deltas (74 ± 55 mmol CO_2 m^{-2} d^{-1})[2]. A recent study using global-scale segmentation found that the

average CO_2 emission rate from small deltas and tidal systems was 16.5 mol m^{-2} y^{-1} (45 mmol CO_2 m^{-2} d^{-1})[25]. This value is very close to that observed in the present study. Tidal systems and small deltas represent over 90% of the estuarine systems of the northern and northeastern regions of Brazil.

Another recent study indicated that upper estuaries are strong sources of CO_2 (106.8 mmol CO_2 m^{-2} d^{-1}), middle estuaries are moderate sources of CO_2 (47.9 mmol CO_2 m^{-2} d^{-1}) and lower estuaries are weak sources of CO_2 (23 mmol CO_2 m^{-2} d^{-1}). These values are very similar to those obtained in our study (85, 67.2 and 23 mmol CO_2 m^{-2} d^{-1}, respectively)[26]. According to the Kruskal-Wallis and Dunn tests, the estuarine groups in this study showed significant differences ($p < 0.05$) among the upper, middle and lower types. Tidal fresh and inner estuaries emit CO_2 to the atmosphere via heterotrophic ecosystem metabolism[9,27]. However, our data (pCO_2 values and CO_2 fluxes) showed high standard deviation values, which complicates comparisons.

We refer to 6 reports indicating that tropical estuaries (<23.5° latitude) exhibit an average emission rate of 23.9 ± 28.5 mol CO_2 m^{-2} d^{-1} (65.4 mmol CO_2 m^{-2} d^{-1}), which is very similar to the values obtained in the present study for the climatic types Af (69.3 mmol CO_2 m^{-2} d^{-1}), Am (60 mmol CO_2 m^{-2} d^{-1}) and Aw (53.7 mmol CO_2 m^{-2} d^{-1}). According to the Kruskal-Wallis and Dunn tests, the climatic groups showed significant differences ($p < 0.05$), primarily between the Af and BSh types. The spatial FCO_2 patterns observed in the northern and northeastern Brazilian estuaries were similar to those observed in tropical regions in other studies, indicating similar
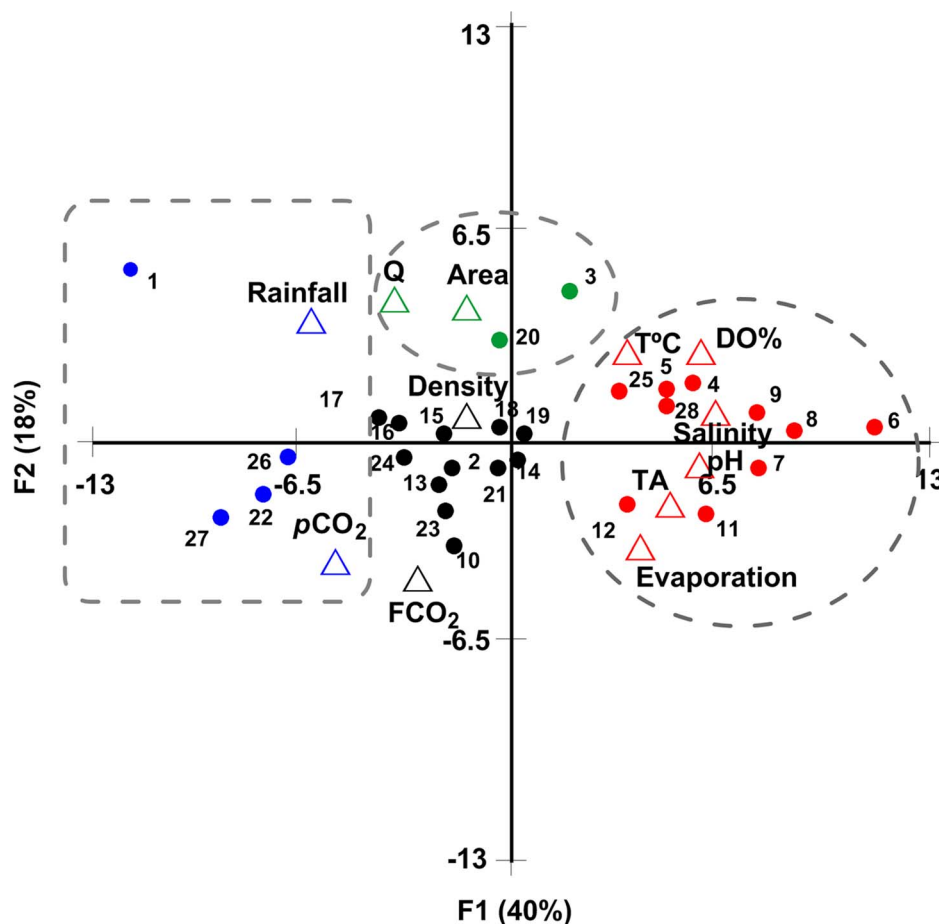
Figure 5 | Graphic representations of the results of the principal component analysis (PCA). The four groups correspond to the four associations: rainfall and pCO_2 (within the square area); fluvial discharge (Q) and estuarine area (within the smaller oval); evaporation, DO%, temperature (T°C), pH, TA and salinity (within the larger oval); and population density and FCO_2 (within the central area of the graph). The parameters are indicated by triangles (Δ), and the estuaries are indicated by filled circles (•).

hydrological and biological processes, with the exception of the *BSh* climatic type. As noted above, the semi-arid estuaries in this region are surrounded by shrimp farms, salt ponds and agricultural areas. The rates of FCO_2 determined for these systems were similar to those determined for the lower estuaries. As can be noted in Fig. 5, the estuaries in this region exhibited positive correlations among salinity, TA, pH and evaporation.

Finally, Brazilian estuaries contribute 1.01 Tg C y^{-1} (52%) less CO_2 to the atmosphere than that reported for Indian estuaries (1.92 Tg C y-1)[24]. However, the estuarine area of the Brazilian systems presented here is 6.4 times lower than that of Indian estuaries. Small deltas and tidal systems worldwide are estimated to contribute 120 Tg C y^{-1} as CO_2 to the atmosphere from an area of 360 × 10^3 km^2[22].

Our study suggests that the estuaries in northern and northeastern Brazil act as sources of CO_2 to the atmospheric. The range of pCO_2 levels observed was similar to that reported for other inner estuaries, except in the case of a few estuaries of the *BSh* climatic type for which lowest levels of pCO_2 were determined.

The FCO_2 observations made in this study contribute to the characterization of humid tropical estuarine systems that previously represented an important geographical information gap.

Methods

Geographic coverage and types of systems studied. The Brazilian coastal zone spans from latitude 4° N to latitude 34° S. Due to the length of the coast, the interface zone from the continent to the ocean includes a wide range of climatic and geographic regions that vary in their hydrologic, geologic, geomorphologic and oceanographic characteristics[28]. The geographic area covered in this study included small deltas, tidal systems and large rivers, which constituted 28 systems along a 17.2° latitudinal band (−0.6°; −47.6° to −17.75°; −39.2°), representing 42% (3,875 km) of the total length of the Brazilian coast (9,198 km). In the northern region, three systems (covering a total area of 2,870 km^2) were studied, whereas in the northeastern region, 25 systems (covering a total area of 1,351.5 km^2) were studied. The population density in the basins adjacent to these systems were <100 inhabitants/km^2 for 12 systems, 100 ≤ inhabitants/km^2 < 1,000 for 13 systems and >1,000 inhabitants/km^2 for 3 systems (Table 1).

According to the Köppen climate classification system[29], 7 of the systems are classified as climate type *Am* (tropical wet climate), 6 systems as type *Af* (tropical rainforest climate), 11 systems as *Aw* (tropical wet and dry or savanna climate) and 4 systems as *BSh* (semi-arid climate). According to this classification system, *tropical climates* and *dry* (*arid and semi-arid*) *climates* are present in our study area (Fig. 1).

According to an estuarine gradient classification system[30], 8 of the systems are characterized as *tidal fresh* and *upper estuary* type, 11 belongs to the *inner estuary* type, 3 to the *middle estuary* type and 6 to the *lower estuary* type (Table 1).

River discharge data were obtained from the database of the Brazilian National Water Agency[31], and demographic data were obtained from a database of the Brazilian Institute of Geography and Statistics[32].

Sampling, analysis and calculation methods. *In situ* measurements were conducted from a boat during 12 continuous months (July 2012–June 2013) in estuarine portions (0.5 ≤ salinity < 35) of the 6 systems of the coast of the state of Pernambuco (−7.55°; −34.8° to −8.85°; −35.1°). Temperature and salinity (conductivity) were measured using a CTD (Sea Bird Electronics SBE911plus® - Washington, USA). Measured salinity was verified via comparison with the chlorinity, which was determined using AgNO$_3$ titration[33]. pH was measured on the NBS scale on board and after sample collection using a pH/ion analyzer 350 and a Ross combination electrode (Orion ®). The precision and the accuracy of the pH measurements were ±0.005 units and 0.1%, respectively. In the laboratory, total alkalinity (TA) was determined using analytical procedures described by the US Geological Survey (USGS) for water samples ('ANC–alkalinity and acid neutralizing capacity') using the inflection point titration method[34]. The precision and accuracy of TA determinations were ±20 μmol kg^{-1} and 5%, respectively. Dissolved inorganic nutrients (phosphate (DIP) and silicate) were analyzed according to Reference 33, after filtration of the samples using 0.47-mm Whatman® GF/C glass fiber filters. The precision was 0.01 μmol for DIP and 0.03 μmol for silicate. The accuracy was ±2% for DIP and ±6% for silicate.

Additionally, we estimated the amount of carbon emissions from 22 estuaries on the Brazilian coast (several months between 2001 and 2012) using measurements of salinity, temperature, phosphate, silicate, dissolved oxygen (DO), alkalinity and pH together with data stored at a monthly resolution from monitoring records of sources linked to states and universities in Brazil. The relative oxygen saturation (DO%) in the water was calculated from the DO concentrations and oxygen solubility in the water at the field temperature and salinity. The apparent oxygen utilization (AOU) was computed using oxygen solubility equations[35].

pCO_2, FCO_2 and DIC were computed using the salinity, temperature, nutrients (phosphate and silicate), pH and TA measurements with dissociation constants given for a salinity range of 0 to 50[36] in the CO_2calc® program[37]. Daily and monthly wind speed and barometric pressure data were obtained from the Brazilian Meteorological Institute (INMET) for stations that were close to the respective estuaries. The molar fraction of atmospheric CO_2 (XCO_2) was obtained from NOAA (http://esrl.noaa.gov) (ppm), and pH_2O = water vapor pressure (μatm) was obtained from Reference 38. The gas transfer rate was calculated using the equation given in Reference 39.

Statistical analyses (regression analyses, t-tests, Spearman's correlation, principal component analysis or PCA and descriptive statistics) were performed using the XLSTAT® 2010 software.

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Author contributions

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