Sea-air CO$_2$ fluxes along the Brazilian continental margin

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ABSTRACT

Measurements of the marine carbonate system on tropical and subtropical continental margins are poorly distributed in space and time, with many uncertainties persisting regarding the role of carbon exchanges at the ocean-atmosphere interface in these areas. To calculate sea-to-air CO$_2$ fluxes in Marine Ecoregions along the Brazilian continental margin (4°N to 34°S), we used data from the Surface Ocean CO$_2$ Atlas (SOCAT v2020), collected up to 400 km from the coast, at the surface (5 m), between 1991 and 2018, with the aim of investigating the role of ecoregions as potential sinks or sources of atmospheric CO$_2$. The temperature and salinity of seawater presented variability in the north-south direction mainly because of the broad latitudinal range, reflecting typical patterns of tropical ($T = 27.4°C ± 1.49; S = 36.4 ± 1.91$) and subtropical waters ($T = 22.8°C ± 3.41; S = 35 ± 2.91$), in addition to the greater or lesser influence of river inputs in each ecoregion. The pCO$_2$ values in the surface waters varied from 121.81 (Amazon) to 478.92 µatm (Eastern), differing significantly between ecoregions and showing an expected decadal increasing trend, both in the atmosphere and in the seawater. The calculated values of CO$_2$ fluxes showed non-homogeneous spatio-temporal variations, from -24.37 mmol m$^{-2}$ d$^{-1}$ (Rio Grande) to 9.87 mmol m$^{-2}$ d$^{-1}$ (Southeastern). Throughout the analyzed time series, we observed that the Northeast, Amazon and Eastern ecoregions acted predominantly as sources of CO$_2$ and the Southeastern ecoregions and, mainly, Rio Grande, acted predominantly as sinks of atmospheric CO$_2$.

Descriptors: Atlantic Ocean, Blue Amazon, Carbonate system, CO$_2$ source or sink, Brazilian marine ecoregions.

INTRODUCTION

Human activities are increasingly releasing large amounts of carbon dioxide (CO$_2$), resulting in an increase in this greenhouse gas in the atmosphere (Jansen et al., 2007; Friedlingstein et al., 2019). Present-day atmospheric concentrations already reached 411.29 ppm (Tans and Keeling, 2020), corresponding to a rise of around 48% compared to the pre-industrial period (Friedlingstein et al., 2020). Only in the last decade, between 6 and 10 Pg-C year$^{-1}$ were emitted from different anthropogenic sources, (Takahashi et al., 2019). The oceans act as an...
important contemporary sink for carbon, absorbing around 27% of the annual anthropogenic CO₂ emissions (Khatiwala et al., 2013; Le Quéré et al., 2013), showing an increasing annual global uptake since pre-industrial period (Khatiwala et al., 2013; Gruber et al., 2019). It is estimated that, if current CO₂ emission rates are maintained in the “business-as-usual” scenario (Shared Socioeconomic Pathway 5-8.5, SSP5-8.5), atmospheric concentrations of this gas may exceed 1,000 ppm by the end of the 21st century.

Continental margins, although corresponding to a small fraction of the area and volume of the ocean, represent around 25% of global primary production and absorb 0.2 PgC of the total of 2.4 ± 0.5 Pg C assimilated annually by the global oceans, despite strong spatial variability (Ito et al., 2016; Laruelle et al., 2018; Roobaert et al., 2019). Long-term analyzes of the sea-air pCO₂ gradient have shown that continental shelves represent a global CO₂ sink, and some regions display a trend to increase atmospheric carbon dioxide absorption (Laruelle et al., 2018). Although there is still much uncertainty concerning the patterns of carbon exchange at the sea-air interface, especially on the tropical and subtropical continental margins, compared to other regions of the global ocean (Chen and Borges, 2009), some studies have been developed to characterize and understand these patterns in different regions of the Brazilian coast, analyzing: local aspects in continental shelf (Ito et al., 2005); estuarine environments (Cotovicz et al., 2020a); areas under strong fluvial influence (Ito et al., 2016; Monteiro et al., 2020); upwelling areas (Oliveira et al., 2019); and coral reefs (Cotovicz et al., 2020b).

The Brazilian continental margin, extending from 4°N to 34°S, includes a broad diversity of oceanographic features (Bernardes et al., 2012). In the northern portion is dominated by a large freshwater input from the Amazon River, generating a plume that covers up to 2,106 km², and can reach from 50°W to 25°W longitude and up to 10°N latitude during the peak flow of the North Equatorial Counter-current (Meade et al., 1985; Probst et al., 1994; Labat et al., 2004; Coynel et al., 2005). The narrow eastern Brazilian continental margin receives a low fluvial input, and has a typically oligotrophic pattern (Pereira et al., 2005). While the southeast Brazilian continental margin (~20°-28°S) presents an important seasonal coastal upwelling system, presenting a stronger stratification during the summer, especially during South Atlantic Central Water (SACW) intrusion events (Pezzi et al., 2009; Pereira et al., 2014). At its southernmost portion, the influence of the Rio de la Plata, which is 5th largest river in the world (Ludwig et al., 1996; Meybeck and Ragu, 2012) and Lagoa dos Patos is highlighted, draining around 200,000 km² of continental area (Möller et al., 2008). Both systems together provide an average input of 25,400 m³s⁻¹ of fresh water to the shelf (Campos et al., 2008; Möller et al., 2008).

The partial pressure of CO₂ (pCO₂, product of the molar fraction of CO₂ and the total mixing pressure (Libes, 2011). High spatial resolution measurements of the pCO₂ in the surface waters in many global coastal regions are performed on several cruises, including ships of opportunity on commercial routes, leading to an increase in the number of CO₂ measurements in recent decades (Sabine et al., 2010). These data are compiled and made available by the Surface Ocean CO₂ Atlas – SOCAT (Bakker et al., 2020), a database with over 28.2 million observations for the 1957–2019 period (Gloege et al., 2022), and with around 172,000 intermittent observations, between the years 1991 and 2018, along the limits of the Brazilian continental margin. The SOCAT dataset was used in the present work aiming at calculating the sea-air CO₂ fluxes along the Brazilian continental margin and investigating the role of the ecoregions as a potential source or sink of atmospheric CO₂, to understand the dynamic ocean-atmosphere in this large geographical area.

METHODS

Study area

The Brazilian continental margin (10,959 km, latitudes ranging from 4°N to 33°S), the so-called “Blue Amazon” (5.7 million km²), includes the Territorial Sea (12 miles from the coast) and the largest Exclusive Economic Zone (Brazilian EEZ) in South America (3.5 million km²), one of the largest on the planet (Bauer et al., 2013; Gerhardinger...
et al., 2018). The main currents along the Brazilian continental shelf are the warm, western boundary Brazil Current, associated with the South Atlantic Subtropical Gyre (Silveira et al., 2000), and the North Brazil Current. Tropical Water is the predominant water mass in the surface, with typically warm (> 18°C) and saline (> 36) waters, due to intense radiation and evaporation (Silveira et al., 2000).

According to the regional classification of Marine Ecoregions of the World (MEOW) (Spalding et al., 2007), the Warm Temperate SW Atlantic comprises the sub-regions S and SE Brazil, the Tropical SW Atlantic includes the sub-regions E and NE Brazil, and the North Brazil Shelf includes the sub-region Amazon (Figure 1). The main coastal upwelling in Brazil is located in the Warm Temperate SW Atlantic. This feature results from a combination of the coastline orientation and NE winds, perpendicular to the continent, promoting the upwelling of the South Atlantic Central Water (SACW), a water mass with temperatures <18°C and salinities <36 (Silveira et al., 2000; Castro et al., 2017). The Tropical SW Atlantic is a region under the predominant influence of oligotrophic oceanic waters, seasonally influenced by the Intertropical Convergence Zone (ITCZ) and El Niño- Southern Oscillation (Araujo et al., 2019; Cotovicz et al., 2020a). In the North Brazil Shelf, the Amazon River plume may reach areas up to 300 km from the coast, seasonally interfering with surface temperature and salinity patterns in this region, with the river volume varying ca. 50% between the dry and rainy seasons (Silva et al., 2010).

![Figure 1. Map of the Brazilian continental margin/Brazilian Exclusive Economic Zone (Blue Amazon) region, considering the boundaries of the ecoregions (Spalding et al., 2007) with the overlap of the SOCAT collection points (black dots = 171,499 observations).](image-url)
The wind regime in the Eastern and North-Eastern coasts is dominated by the south-easterly and easterly trade winds. Along the eastern coast occurs a zone of divergence between the trade winds, and northeastern winds blow to the south of this zone. On the Brazilian North coast, northeasterly trades prevail and, in the South, the easterly and south-easterly winds blow during fall and winter (April–September) and the northeasterly winds prevail during spring and summer (September–February) (Leão et al., 2010).

**DATA PROCESSING**

Carbon system parameters used in this study were obtained from Surface Ocean CO$_2$ Atlas (SOCAT v2020), which gathers data on fugacity data (fCO$_2$), temperature, salinity, atmospheric pressure, and sea level pressure, from continuous measurements *in situ*, from scientific and opportunity cruises (Bakker et al., 2020). The data were downloaded from https://www.socat.info/index.php/data-access/, last access: 13 January 2022. Here we used data collected along the Brazilian continental margin, up to 400 km from the coast, in surface waters (5 m), between 1991 and 2018, when there are consistent *in situ* data for calculating the CO$_2$ fluxes in the five ecoregions, although with some spatial or temporal gaps. Instantaneous wind speed data were obtained from the Cross-Calibrated Multi-Platform - CCMP (www.remss.com/measurements/ccmp., last access: 26 August 2022) (Atlas et al., 2011; Wentz et al., 2015; Mears et al., 2019), using the geographical coordinates of the SOCAT sampling points.

Fugacity data (fCO$_2$) were converted into CO$_2$ partial pressure, and sea-air CO$_2$ fluxes, using equations widely used in many studies (e.g. Rödenbeck et al., 2013; Laruelle et al., 2018; Araujo et al., 2019; Monteiro et al., 2020). For the sea-air CO$_2$ flux (FCO$_2$) calculation we use the equation:

\[
[1] \text{FCO}_2 = kCO_2 \times \text{SCO}_2 \times \Delta pCO_2 \text{ seawater-air}
\]

Its components are:

\[
[1.1] kCO_2 = 0.251 \times u^2 \times (Sc /660)^{1/2}
\]

Where: \(K\) = gas transfer speed; \(u\) (m s$^{-1}$) = wind speed data CCMP (Atlas et al., 2011; Wentz et al., 2015; Mears et al., 2019); \(Sc\) (Schmidt’s number) = 2039.2 – 125.62 \times T + 3.6276 \times T^2 – 0.043219 \times T^3 (Wanninkhof, 2014).

\[
[1.2] \text{SCO}_2 = \exp (A1 + A2 \times (100/T) + A3 \times \log (T/100) + \text{Sal} (B1 +B2 \times (T/100) + B3 \times (T/100)^2))
\]

Where: \(A1 = -60.2409; A2 = 93.4517; A3 = 23.3585; B1 = 0.023517; B2 = -0.023656; B3 = 0.0047036\) and \(T = \text{Kelvin temperature}\) Sal = salinity (Weiss, 1974).

\[
[1.3] \Delta pCO_2 \text{ seawater-air} = pCO_2 \text{ seawater} - pCO_2 \text{ air}
\]

\[
[1.3.1] pCO_2 \text{ seawater} = fCO_2 (1.00436 - 4.66910^{-5} \text{SST})
\]

\[
[1.3.2] pCO_2 \text{ air} = XCO_2 (Pbaro - Psw)
\]

Where: \(Psw = \exp (24.4543 – 67.4509 (100/T) – 4.8489 \log((T/100)) – 0.0005445 \times \text{Sal}\)

\(XCO_2 = \text{CO}_2\) concentration average dry air (xCO$_2$ \(\mu\text{mol.mol}^{-1}\)); *Pbaro = sea level pressure (hPa); Psw = atmospheric pressure (hPa), and *T = Kelvin temperature (Weiss and Price, 1980).

**STATISTICAL ANALYSES**

To assess the temporal trend (1990 - 2018) of CO$_2$ fluxes along the Brazilian continental margin, we investigated 26 years of observations available from the SOCAT. After verifying the non-parametric distribution of the data set (Shapiro-Wilk test), the Kruskal-Wallis test and a post hoc Wilcoxon rank test were applied, in order to perform the variance analysis between periods with CO$_2$ fluxes data available concurrently for the five ecoregions.

The annual trends analysis of CO$_2$ fluxes was performed using linear regressions, calculated considering the time series of data for each ecoregion separately. Mann-Kendall test was used to verify the temporal variations significance (\(\alpha = 0.05\)). Based on the temperature variations, the following two seasons were delimited: a) warm season (i.e. temperatures above the time series mean) and b) cold season (i.e. temperatures
below the time series mean). From this delimitation, an analysis of variance (Mann-Whitney test) was performed to verify the occurrence of significant variations in CO₂ fluxes between these seasons. All statistical analyses were performed in the R environment (R Core Team 2022).

RESULTS

SST, SSS and wind speed in the Brazilian coastal ecoregions

Surface seawater (5 m) temperature and salinity (Figure 2) reflected the geographical (north-south), and the low seasonal variability, typical of tropical (T = 27.4°C±1.49; S = 36.4±1.91) and subtropical (T = 22.8°C±3.41; S = 35±2.91) waters. Likewise, for wind speed a low variation pattern was observed between the different coastal regions (Table 1). Lower salinities in some regions result from the influence of fluvial input on the coast, with a greater range of variation recorded in the Amazon ecoregion, under strong influence of the Amazon River plume, and a greater thermal amplitude in the Rio Grande ecoregion, reflecting of the La Plata River and the Patos Lagoon inputs (Figure S1).

Considering the water average temperature throughout the time series data, periods of warmer and cooler waters were delimited, for each ecoregion (Figure 3). Thus, the Amazon ecoregion had higher water temperature in the period from May to September (mean = 28.76 ±0.6°C) and water, average 1°C colder, between November and April (27.76±0.42°C). In the Eastern ecoregion, the warmest period was between December and May (27.42±1.26°C), and the coldest between July and November (24.94±1.42°C). In the Northeast ecoregion, the warmest waters period occurred between January and June (28.35±0.59°C), with slightly cooler water, between July and December (27.15±0.71°C). The period from December to April (26.06±1.41°C) corresponded to the warmest water months in the Southern ecoregion, and from May to November the lowest water temperatures were recorded (22.51±1.32°C). And in the Rio Grande ecoregion, the period corresponding from December to March (23.83±1.91°C) shows the period of warmer waters, with waters on average 5°C cooler between May and November (18.23±2.16°C).

Carbonate system (pCO₂ and CO₂ fluxes) in the Brazilian coastal ecoregions

Despite the large amount of SOCAT data points (171,499 observations), there are several spatial and temporal gaps. After data filtering, we achieved consistent temporal coverage for the

Figure 2. T-S diagram. Variation of temperature and salinity in surface water (= 5m) in the ecoregions of the Brazilian continental margin. Amazon ecoregion (large salinity range under strong influence of the Amazon River plume); Northeastern, Eastern and Southeastern ecoregions (typically coastal and tropical water), and Rio Grande ecoregion (wide temperature and salinity ranges under influence of the La Plata River and the Patos Lagoon inputs).
Table 1. Variations (minimum, maximum, mean and standard deviation) of Sea Surface Temperature (SST*) (°C), Sea Surface Salinity (SSS*) and Wind speed** (m s⁻¹) in each ecoregion of the Brazilian continental margin, obtained from the Surface Ocean CO₂ Atlas (SOCAT*) and Cross-Calibrated Multi-Platform (CCMP**).

<table>
<thead>
<tr>
<th>Ecoregion</th>
<th>Period</th>
<th>SST</th>
<th>SSS</th>
<th>Wind speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amazon</td>
<td>1993 - 2018</td>
<td>26.32 - 30.18 (28.23 ± 0.71)</td>
<td>16.57 - 36.54 (33.75 ± 4.24)</td>
<td>2.00 - 10.1 (6.46 ± 2.26)</td>
</tr>
<tr>
<td>Northeastern</td>
<td>1991 - 2018</td>
<td>24.98 - 30.40 (27.71 ± 0.89)</td>
<td>33.63 - 37.52 (36.21 ± 0.52)</td>
<td>2.01 - 10.7 (6.18 ± 1.72)</td>
</tr>
<tr>
<td>Southeastern</td>
<td>1991 - 2018</td>
<td>17.58 - 29.46 (24.03 ± 2.22)</td>
<td>24.96 - 37.44 (36.03 ± 1.35)</td>
<td>2.48 - 9.58 (6.04 ± 1.18)</td>
</tr>
<tr>
<td>Eastern</td>
<td>1991 - 2018</td>
<td>19.29 - 29.45 (26.45 ± 1.79)</td>
<td>34.23 - 37.76 (37.09 ± 0.40)</td>
<td>2.48 - 9.58 (6.04 ± 1.18)</td>
</tr>
<tr>
<td>Rio Grande</td>
<td>1991 - 2018</td>
<td>12.87 - 27.42 (20.71 ± 3.46)</td>
<td>19.70 - 37.05 (33.66 ± 3.44)</td>
<td>3.88 - 9.11 (7.22 ± 1.08)</td>
</tr>
</tbody>
</table>

Brazilian coastal ecoregions, starting in 1991. However, only in the years 2004, 2006, 2007, 2016, 2017 and 2018 data were available for all five ecoregions (Figure S2).

The pCO₂ values in the surface seawaters varied between 121.81 (Amazon) and 478.92 µatm (Eastern). The Kruskal-Wallis test showed significant differences for pCO₂ among ecoregions (p < 0.001). In the Amazon ecoregion the variation registered for surface seawater pCO₂ was from 121.81 to 458.62 (369.99 ± 66.64) µatm, presenting a non-significant time trend (Kendall’s tau = -0.017; p = 0.944), with annual reduction of -0.34 µatm year⁻¹ (Figure 4). Therefore, a trend opposite to that of pCO₂ atmospheric (Kendall’s tau = 1; p < 0.001), whose increase was 1.87 µatm year⁻¹ during the analyzed period (Figure 5). In the Eastern ecoregion, the pCO₂ seawater ranged between 305.30 and 478.92 (390.91 ± 18.17) µatm, presenting a significant time trend (Kendall’s tau = 0.6; p < 0.001), with annual increase of 1.5 µatm year⁻¹ (Figure 4). In the same way as atmospheric pCO₂ (Kendall’s tau = 0.96; p < 0.001), whose increase was 1.95 µatm year⁻¹ (Figure 5).

The variation of the pCO₂ seawater in the Northeastern ecoregion was from 328.81 to 445.64 (394.96 ± 18.12) µatm, presenting a significant time trend (Kendall’s tau = 0.776; p < 0.001), with annual increase of 1.62 µatm year⁻¹ (Figure 4), similar to that observed for atmospheric pCO₂ (Kendall’s tau = 0.98; p < 0.001), whose increase was 1.91 µatm year⁻¹ during the analyzed period (Figure 5). The temporal trend was also significant (Kendall’s tau = 0.581; p = 0.0001) in the Southeastern ecoregion, ranging from 257.33 to 299.18 (381.28 ± 25.34) µatm. With annual increase of 1.93 µatm year⁻¹ (Figure 4), very similar to that observed for atmospheric pCO₂ (Kendall’s tau = 0.98; p < 0.001).
tau = 0.95; p < 0.001), whose increase was 1.95 μatm year⁻¹ (Figure 5).

Rio Grande ecoregion was the only one with the highest annual increment of pCO₂ in seawater (1.79 μatm yr⁻¹), which varied between 143.86 and 437.72 (359.85 ± 35.99) μatm, than in the atmosphere (0.23 μatm year⁻¹). Both showed significant trends (seawater pCO₂: Kendall’s tau = 0.604; p = 0.0031 and atmospheric pCO₂: Kendall’s tau = 0.889; p = 0.0012) (Figures 4, 5), although with very low adjustments, as recorded for temporal trends of all the other four ecoregions, in the analyzed period.

The sea-air CO₂ fluxes along the Brazilian continental margin ranged from -24.37 mmol m⁻²d⁻¹ (Rio Grande) to 9.87 mmol m⁻²d⁻¹ (Southeastern), differing significantly among ecoregions (p < 0.05), except between Amazon and Northeastern (Wilcoxon test, p = 0.45). Most values ranged between -10.0 and 10.0 mmol m⁻²d⁻¹ (Figure 6).

The largest variation amplitudes of CO₂ fluxes along the analyzed time series were recorded in the ecoregions Rio Grande (-24.37 to 7.11 mmol m⁻²d⁻¹) and Amazon (-20.64 to 6.03 mmol m⁻²d⁻¹). In the ecoregions Eastern (-5.72 to 9.85
mmol m$^{-2}$ d$^{-1}$), Southeastern (-5.97 to 9.87 mmol m$^{-2}$ d$^{-1}$) and, mainly Northeastern (-4.29 to 6.71 mmol m$^{-2}$ d$^{-1}$), the variation amplitudes of CO$_2$ fluxes were smaller.

The calculated ocean-atmosphere CO$_2$ fluxes were variable, non-homogeneously distributed along the Brazilian continental margin (Figure 7). We observed that the highest means of positive CO$_2$ flux occurred, respectively, in the Northeast (1.26 ± 1.56 mmol m$^{-2}$ d$^{-1}$), Amazon (0.72 ± 3.58 mmol m$^{-2}$ d$^{-1}$) and Eastern (0.66 ± 1.34 mmol m$^{-2}$ d$^{-1}$). The three acted, predominantly, as sources of CO$_2$ to the atmosphere (Figure 8). While the Southeastern ecoregion, despite the negative mean value of CO$_2$ flux (-0.16 ± 1.58 mmol m$^{-2}$ d$^{-1}$), showed alternation between short periods as a source, and longer periods as an atmospheric CO$_2$ sink (Figure 8). In this context, only the Rio Grande ecoregion (-2.49 ± 3.70 mmol m$^{-2}$ d$^{-1}$) acted predominantly as an atmospheric CO$_2$ sink (Figure 8).

**Temporal trends in pCO$_2$ and CO$_2$ fluxes along the Brazilian continental margin**

Decadal analysis (1990 - 2018) of pCO2 trends presented similar values of pCO$_2$ increment in the atmosphere and seawater, observing an increase in these values throughout the time series. In the 1990s, atmospheric pCO$_2$ showed a positive trend of 1.41 µatm yr$^{-1}$ (Kendall’s tau = 0.4; p = 0.46) and the trend of pCO$_2$ seawater was 1.02 µatm yr$^{-1}$ (Kendall’s tau = 0.389; p = 0.175). In the following decade, pCO2 values were 1.74 µatm year$^{-1}$ (Kendall’s tau = 1; p = 0.0008) in the atmosphere, and 1.69 µatm year$^{-1}$ (Kendall’s tau = 0.2; p = 0.474) in the seawater. And between 2011 and 2018, for the first time along the analyzed time series, the pCO$_2$ seawater (2.78 µatm yr$^{-1}$; Kendall’s tau = 0.722; p = 0.009) was higher than the atmospheric values (2.49 µatm yr$^{-1}$; Kendall’s tau = 1; p = 0.027) (Figure 4, 5).

Generally, the Brazilian continental margin acted as a CO$_2$ source (Figure 7), presented, in average, trend of positive CO$_2$ flux (0.05 mmol year$^{-1}$; Kendall’s tau = 0.0714; p = 0.901) until the 2000s, changing to act as an atmospheric CO$_2$ sink, in the two following decades. Between 2001 and 2010 the CO$_2$ flux presented a negative trend of -0.03 mmol year$^{-1}$ (Kendall’s tau = -0.244; p = 0.37) and in the last period of available data (2011 to 2018) this trend was of -0.05 mmol year$^{-1}$ (Kendall’s tau = -0.214; p = 0.53). Highlighting that the temporal trends in the three decades were not significant and showed a low linear adjustment (Figure 9).

Considering seasonal variations, we observed that there were significant differences (p< 0.001) in seawater pCO$_2$ values between the warmer and colder periods, in the five ecoregions. In the
Amazon ecoregion, the seawater pCO$_2$ average was higher in the coldest period (350.64 ±80.67 μatm; November to April), than during the warmer period (350.64 ±80.47 μatm; May to September). In the other ecoregions, the opposite pattern was registered, with the highest seawater pCO$_2$ averages recorded in the warmer periods: Eastern (394.14 ±17.83 μatm; December to May/386.63 ±19.25 μatm; June to November); Northeastern (400.05 ±17.21 μatm; January to Juny/393.72 ±19.02 μatm; July to December); Southeastern (390.53 ±24.49 μatm; December to April/375.09 ±23.85 μatm; May to November) and Rio Grande (379.78 ±23.12 μatm; December to March/349.55 ±37.17 μatm; May to November).

The analysis of CO$_2$ fluxes, considering this seasonality, presented positive average values in the Amazon ecoregion (1.81 ± 3.04 mmol year$^{-1}$) in the coldest months. Indicating that the area acted as a CO$_2$ source in this period and as an atmospheric CO$_2$ sink in the warmer period (-0.50 ±3.74 mmol year$^{-1}$) (Figure 8). On the other hand, the Southeastern

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Figure 7. CO$_2$ fluxes variation indicating source (positive values) or sink (negative values) areas, along the Brazilian continental margin. *Pixel size = 1° (approximately 100 km).
CO₂ fluxes in Brazilian marine ecoregions
Ocean and Coastal Research 2023, v71(suppl 2):e23017

Figure 8. CO₂ fluxes variation (1991 - 2019) in the ecoregions of the Brazilian continental margin. a- Amazon (warmest period: May - September; coldest period: November - April); b- Eastern (warmest period: December - May; coldest period: July - November); c- Northeastern (warmest period: January - June; coldest period: July - December); d- Southeastern (warmest period: December - April; coldest period: May - November); e- Rio Grande (warmest period: December - March; coldest period: May - November).

The Northeastern and Eastern ecoregions acted predominantly as CO₂ sources in both seasonal periods, with an average variation of CO₂ fluxes between 1.23 (±1.80) mmol year⁻¹ (cold) and 1.29 (±1.22) mmol year⁻¹ (warm) in the Northeastern ecoregion (Figure 8). And between 0.1 (±1.37) mmol year⁻¹ (cold) and 1.08 (±1.12) mmol year⁻¹ (warm) in the Eastern ecoregion (Figure 8). Only the Rio Grande ecoregion acted as an atmospheric CO₂ sink throughout the entire period, with average fluxes between -0.74 (±2.53) mmol year⁻¹, in the warm period, and -3.17 (±3.86) mmol year⁻¹, in the coldest period (Figure 8).
Discussion

The variations observed in the dataset along the continental margin in surface temperature and salinity reflect the typical variability of this region. Around the NE, E and SE regions there is a dominance of Tropical Water (Stramma and Schott, 1999), while at the Amazon region there is a strong influence of the Amazon River plume (lower salinity), which may extend up to hundreds of kilometres transported by the North Brazil Current and the North Equatorial Countercurrent. Tropical precipitation also affects salinity in this region.

The northeast and eastern Brazilian continental margin are narrow, receiving low riverine input, and typically oligotrophic, influenced in the inner shelf by the warm and low salinity Coastal Water \((T>20^\circ C \text{ and } S<35)\), while on the outer shelf the saltier Tropical Water \((T>20^\circ C \text{ and } S>36.4)\) of the Brazil Current (BC) is observed at the surface (Pereira et al., 2005). Further south, the continental margin broadens, and the inner shelf is characterized by the Coastal Water (CW) while at the outer shelf the Brazil Current transports Tropical Water (TW) at surface and South Atlantic Central Water (SACW) at pycnocline level (Calado et al., 2010; Rocha et al., 2014). The coastal upwelling areas around the Cabo Frio and Cabo São Tomé \((22-23^\circ S)\) are a source of variability to surface temperature and salinity. South of Cabo Frio, the South Brazil Bight (SBB) shows stronger stratification during summer, especially during SACW intrusion events (Brandini et al., 2013).

During winter, the SBB water column is mixed due to winds, and at its southern portion (around 27°-28°S latitude) there may be intrusions from less saline and colder waters from the La Plata River plume and the Patos Lagoon (Piola et al., 2008). The buoyant La Plata plume flows northwards close to the shore, especially during winter pushed by stronger southwestern winds, creating a lateral salinity gradient (Campos et al., 2008; Ciotti et al., 2014). The mixing of the La Plata River plume and the Tropical Water on the shelf forms a front called Subtropical Shelf Water (Piola et al., 2008).

Despite the marked spatio-temporal gaps in the carbonate system measurements, we observed a spatial trend of pCO\(_2\) values increasing and the average CO\(_2\) fluxes in the south-north direction along the Brazilian coast, as well as during warmer periods. This pattern is consistent with the temperature marked influence on the dynamics of the carbonate system, affecting the CO\(_2\) solubility (Landschützer et al., 2014; Heinze et al., 2015). The Amazon ecoregion showed the opposite pattern, with increasing both pCO\(_2\) values and average ocean-atmosphere CO\(_2\) fluxes during the coldest periods. Here we highlight the marked influence of Amazon River inputs, widely discussed as a determining factor in the carbonate system variability, between periods of high and low discharge (Körtzinger, 2003; Ibánhez et al., 2016; Landschützer et al., 2016; Lefèvre et al., 2017; Araújo et al., 2019). The area under direct influence of the Amazon River is associated with i) large surface pCO\(_2\) supersaturation area very close to the river mouth (Abril et al., 2013; Cunha et al., 2013), and ii) an area strongly undersaturated with respect to atmospheric CO\(_2\) associated with the Amazon River plume (at latitude 10°N, longitude 50°W-48°W (Körtzinger et al., 2003; Lefèvre et al., 2017; Araújo et al., 2019). This local CO\(_2\) sink is due to a combination of physical (mixing effect of river- and seawater in the plume) and biological (production in the plume) effects. The control exerted over biological processes in the area may have an opposite effect to the temperature (Heinze et al., 2015; Mu et al., 2021), however those were not assessed in the present study.

Many robust data series has demonstrated the indisputable global increase in atmospheric CO\(_2\) over the years (Jansen et al., 2007; Khatiwala et al., 2013; Friedlingstein et al., 2019; Gruber et al., 2019; Takahashi et al., 2019; Tans and Keeling, 2020). This corroborates the temporal trends recorded between 1990 and 2018 on the Brazilian coast, where we observed a decadal increase in atmospheric pCO\(_2\), with a high linear adjustment \((R^2 > 0.75)\), increasing in the same proportion in the seawater. The temporal CO\(_2\) fluxes trends presented, in the first study period (1990 - 2000), an average positive sign, indicating the role of coastal waters as a CO\(_2\) source. In the following decades (2001-2010; 2011-2018), negative temporal trends were recorded, thus characterizing
the area as an atmospheric CO$_2$ sink. Based on an extensive literature review on CO$_2$ fluxes along the Brazilian continental shelf, Oliveira et al. 2022 found evidence of a latitudinal variation in source/sink behavior, observing the North-Northeast as mainly CO$_2$ source areas, the Southeast region acting as a weak CO$_2$ source, and in the southern region, there is a tendency towards a permanent CO$_2$ sink. These patterns may vary over time, depending on local oceanographic and biological processes, and different anthropogenic pressures (e.g. Padin et al., 2010; Cotovicz et al., 2019; Cotovicz et al., 2020b; Marotta et al., 2020; Cotovicz et al., 2021; Valerio et al., 2021; Carvalho et al., 2022).

Although the oceans act as a global CO$_2$ sink, (Padin et al., 2010; Laruelle et al., 2018; Roobaert et al., 2019) this behavior is highly variable on continental margins (e.g. Ito et al., 2005; Jiang et al., 2008; Chen et al., 2013; Carvalho et al., 2017; Araújo et al., 2019), similar to what we observed along the Brazilian continental margin. The assessment of the role of ecoregions as sources or sinks of atmospheric CO$_2$, showed a spatio-temporal dynamics potentially justified by different regional processes. According to Cai et al., (2020), these processes include river inputs, coastal circulation, and spatial and seasonal temperature variations.

In the Amazon ecoregion, our results recorded the highest seasonal range of pCO$_2$ in coastal waters. This high variability results directly or indirectly from the discharge of the Amazon River, evidenced by the broad salinity range (Figure 2), showing the mix of the Amazon River plume with the oceanic water, and the pattern of pCO$_2$ supersaturation in surface waters, close to the river mouth (Abril et al., 2014). Additionally, our results highlight the importance of the Amazon River plume, which creates a regional CO$_2$ sink off the coast (e.g. Lefèvre et al., 2010; Iñáñez et al., 2016; Araújo et al., 2019). Considering the SST seasonality, we identified that the area alternately acted as a CO$_2$ source, in the coldest periods, and as a CO$_2$ sink, in the warmest periods.

In the Northeastern and Eastern ecoregions continuum, the continental shelf is narrow, and typically oligotrophic, receiving low fluvial input, predominantly Coastal Water influenced, warm (T > 20°C) and low salinity (S < 35), on the inner shelf. While on the outer shelf the Brazil Current carries Tropical Water (T > 20°C and S > 36.4) at the surface (Pereira et al., 2005; Calado et al., 2010; Rocha et al., 2014). Seasonal variations are less marked, thus reflecting lower average variation in CO$_2$ fluxes, but increasing the positive sign (CO$_2$ source) in warmer periods. In the transition zone between semi-arid and more humid areas, on the northeast coast of Brazil, Carvalho et al. (2017) recorded seawater CO$_2$ saturation, considering the local hydrological and rainfall conditions, also showing the region’s role as a CO$_2$ source to the atmosphere. The same behavior registered by Cotovicz et al. (2020b), who observed higher CO$_2$ emissions in coral reef areas, when compared to regions close to the coast, and offshore.

According to Oliveira et al. (2019), in the Southeastern ecoregion, ocean-atmosphere CO$_2$ fluxes are highly dependent on local oceanographic and meteorological conditions. In these region the upwelling system between Cabo São Tomé and Cabo Frio (22° - 23°S) stands out, which, which transports cold waters, rich in nutrients, to the surface, providing an increment in local primary productivity during the summer (Moser et al., 2014). In these coastal upwelling regions, surface ocean pCO$_2$ values are usually higher, as a result of upwelled, CO$_2$-enriched subsurface waters (Ito et al. 2016). It is possible to assume, therefore, that the role of this region as a CO$_2$ source in the warmer periods, as we have recorded, derives both from the input of waters that already arrive rich in CO$_2$, and from the intensification of phytoplankton respiration (Borges et al., 2005; Roy-Barman and Jeandeal, 2016).

Rio Grande ecoregion was the only one that presented atmospheric CO$_2$ sink behavior throughout the analyzed time series. This region, located in the southernmost portion of the Brazilian continental margin, receives large water input of the La Plata River, as well as Patos Lagon, typically colder waters, in addition to the influence of the South Atlantic Central Water (SACW). The SACW upwelling, through mesoscale processes, brings additional cooler, nutrient-rich waters to the surface (Pezzi et al., 2009). Thus, this region presents...
thermal gradients that are highly variable in time and space (Souza and Robinson, 2004). Along with the fluvial plume dispersion on the continental shelf, the SACW upwelling enhances local primary productivity (Piola et al., 2000; Möller et al., 2008), especially in the austral winter and spring months (Ciotti et al., 1995). Both processes are potentially responsible for the increased CO$_2$ sink in the area during the coldest period.

CONCLUSIONS

This study covered almost 40° in latitude along the Brazilian margin. The regional division adopted here highlights the dominant biogeographic parameters such as upwelling, freshwater input, temperature, currents or coastal complexity, in the different ecoregions. The water salinity and temperature variations represented a characteristic pattern of north-south variation. In addition to the low seasonality, typical of tropical or subtropical waters, reflecting the greater or lesser influence of river inputs in each ecoregion.

Through the time series analysis of the surface water masses, we could observe the general increasing trend in pCO$_2$, both in the atmosphere and in the seawater. Over shelf and margin areas there is a strong component of biological control in pCO$_2$, especially in the inner shelf and coastal regions such as bays and estuaries. Non-homogeneous sea-to-air CO$_2$ fluxes varied from predominant CO$_2$ sources in the Amazon, Northeast, and East ecoregions, to a predominant atmospheric CO$_2$ sink southwards, especially in the Rio Grande ecoregion. We thus observe a spatial gradient of change from ocean source areas to atmospheric CO$_2$ sink areas from north to south, along the Brazilian continental margin.

Despite the large volume of data available, temporal gaps are common in SOCAT, as data are usually collected during trade routes of opportunity vessels, which occur mainly in summer (Wang et al., 2017). The spatial resolution of observations in certain regions of the Atlantic is also limited, compared to other regions of the global ocean (Sabine et al., 2010). Thus, we believe it is important to highlight the need to invest in scientific cruises and more ships of opportunity to improve the sampling coverage. This will allow more robust analyses of the marine carbonate system in the tropical and south Atlantic continental margins.

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AUTHOR CONTRIBUTIONS

H.M.J.A.: Conceptualization; Investigation; Methodology; Software; Formal Analysis; Writing – original draft; Writing – review & editing;
D.S.B.R.: Methodology; Software; Formal Analysis; Writing – review & editing;
F.R.P., G.A.O.M.: Conceptualization; Writing – review & editing;
M.C.A.F.: Resources; Project Administration; Funding Acquisition; Writing – review & editing.
L.C.C.: Supervision; Conceptualization; Investigation; Methodology; Writing – review & editing.

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