Air–sea CO₂ fluxes for the Brazilian northeast continental shelf in a climatic transition region

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A B S T R A C T

Oceanographic cruises were carried out in October 2012 (3°S–5°S and 38.5°W–35.5°W) and in September 2014 (1°S–4°S and 43°W–37°W), measuring atmospheric and sea surface CO₂ fugacity (fCO₂) underway in the northeast coast of Brazil. Sea surface water samples were also collected for chlorophyll a, nutrients and DOC analysis. During the second cruise, the sampling area covered a transition between semi-arid to more humid areas of the coast, with different hydrologic and rainfall regimes. The seawater (fCO₂)sw in October 2012, was in average 400.9 ± 7.3 μatm and 391.1 ± 6.3 μatm in September 2014. For the atmosphere, the fCO₂air in October 2012 was 375.8 ± 2.0 μatm and in September 2014, 368.9 ± 2.2 μatm. The super-saturation of the seawater in relation to the atmosphere indicates a source of CO₂ to the atmosphere. The entire study area presents oligotrophic conditions. Despite the low concentrations, Chl a and nutrients presented significant influence on fCO₂sw, particularly in the westernmost and more humid part of the northeast coast, where river fluxes are three orders of magnitude larger than eastern rivers and rainfall events are more intense and constant. fCO₂sw spatial distribution presented homogeneity along the same transect and longitudinal heterogeneity, between east and west, reinforcing the hypothesis of transition between two regions of different behaviour. The fCO₂ at the eastern portion was controlled by parameters such as temperature and salinity. At the western portion, fCO₂sw was influenced by nutrient and Chl a. Calculated instantaneous CO₂ flux ranged from +1.66 to +7.24 mmol m⁻² d⁻¹ in the first cruise and +0.89 to +14.62 mmol m⁻² d⁻¹ in the second cruise.

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1. Introduction

Anthropogenic CO₂ emissions to the atmosphere are increasing at a steady rate. The ocean and the terrestrial biosphere absorb a great part of these emissions (Sabine et al., 2004; Canadell et al., 2007). Robust CO₂ climatology (Takahashi et al., 2002; Takahashi et al., 2009) reveals a heterogeneous behaviour, with higher latitudes acting as a sink of CO₂ and lower latitudes acting as a source of CO₂ to the atmosphere. However, the ocean margins are not computed in this analysis and the role of the costal oceans is not well elucidated. There is a debate about coastal CO₂ distribution (Bauer et al., 2013) and many studies suggest the importance of these regions in carbon budgets and CO₂ fluxes (Tsunogai et al., 1999; Cai et al., 2006; Laruelle et al., 2010; Laruelle et al., 2014; Gruber, 2015).

The coastal waters represent a link between terrestrial and oceanic systems, receiving large amount of continental material through river discharges and groundwater, as well as by exchanges between the atmosphere, sediments and the open ocean. Though it represents a small portion of the total oceanic area, it consists in a major contribution to the global carbon cycle and thus, should not be ignored in the carbon budgets (Borges et al., 2005; Chen and Borges, 2009).

Continental margins tend to show greater space and time variability than most remote regions in the oceans and receive more pressure from human activities. Land use and water resources can also alter coastal systems significantly (Jiang et al., 2013). However, coastal oceans are often misrepresented in the global carbon balance. Many studies, however, have shown interest for these areas and their carbon transfer mechanisms in the ocean-atmosphere interface, which has helped to understand the role of continental margins in the CO₂ fluxes (Chen et al., 2013 and references therein).

There are many studies in the temperate systems and only a few studies in tropical ones. Previous measurements in the tropical Atlantic
concluded that it is generally a source of CO₂ to the atmosphere (Andrié et al., 1986; Goyet et al., 1998). Some of its regions represent CO₂ sinks due to the Amazon River discharge causing strong biological activity and CO₂ uptake (Ternon et al., 2000; Körtzinger, 2003; Cooley and Yager, 2006; Ibánhez et al., 2016).

Earlier studies have reported few measurements conducted in the coastal zone and more specifically at the Brazilian coast. The scarcity of estimates of air-sea CO₂ fluxes in regions of the Brazilian continental shelf and the need to understand the effects of climate change on carbon cycle has led to great efforts to measure fCO₂. During the ‘Ocean Circulation in the Southwest Atlantic Region’ program (COROAS), fCO₂ measurements performed in the Brazilian Southwest region contributed to a better understanding of the role of continental shelf in the ocean carbon cycle (Ito et al., 2005).

In this study, fCO₂ underway measurements were made in the Brazilian Equatorial Northeast coastal zone from about 5°S to 0°S, as an effort to contribute with oceanographic cruises performed to better understand the fCO₂ variability in this region.

2. The study area

This study concerns the Brazilian Equatorial Northeast continental shelf (Fig. 1), which is narrow, open to the ocean and oligotrophic. In the Northeast of Brazil, semi-arid climate has led to the building of dams, reducing continental run-off and therefore, inputs for the primary productivity in the coastal ocean.

The rainy season usually extends from January to June and the months of July to December mark the dry season. Monthly mean rainfall values (mm) for the years of 2012 and 2014 were below the expected for the period, when compared to the historical mean for the years of (2000 – 2010) showing a tendency of prolonged drought. Regional rivers such as the Jaguaribe, the Parnaíba and the rivers contributors to São Marcos Bay (SMB) are strongly influenced by climatic seasonality. Average annual rainfall for the Jaguaribe and Parnaíba rivers are respectively: 80 and 91.6 mm. The Parnaíba basin characterizes a transition between the Brazilian northeastern semi-arid region, with intermittent rivers, and the Amazon, where high rainfall and perennial rivers prevail. For the SMB region, this average is about two times higher, 191.3 mm, representing a more humid coastal area. (Fig. 2).

Trade winds from the SE dominate during the dry season, when wind speed is maximum and associated with the lowest temperature, when this study was performed.

Assessments developed by REVIZEE (‘Avaliação do Potencial Sustentável de Recursos Vivos na Zona Econômica Exclusiva’) and JOPS-II (‘Brazil-German Joint Oceanographic Projects’), pointed out that from the Parnaíba River towards the SMB, climatic conditions change from semi-arid to humid with strongest rainfall periods, tide range changes from meso to macro tides, the shelf becomes wider, with upwelling events and higher primary production (Class I). It represents the passage from the so characterized East Brazil shelf Large Marine Ecosystem (LME) to the North Brazil shelf LME (Knoppers et al., 1999; Ekau and Knoppers, 2003).

3. Methods

3.1. Oceanographic cruises and sampling

The first cruise started in October 19th 2012, collecting samples along 57 stations distributed in 12 transects perpendicular to the coast and returned in October 26th 2012. It covered an area of approximately 13,000 km², from latitude 3°S to 5°S and longitude 35.5°W to 38.5°W. The sampling grid in Fig. 3 included the continental shelf between the isobaths of 10 to 1000 m. This area represents a narrow portion in relation to other Brazilian continental margins, inserted in a typical oligotrophic system, with tropical dry to semi-arid climatic conditions. It aimed to obtain a first screening of the area in relation to fCO₂ in the air and in the seawater, and to observe the variability between the inner and external shelves as well as the influence of rivers and continental discharges.

The second cruise, carried out from September 7th to the 14th, 2014, proposed a broader sampling grid of the Brazilian continental shelf westwards. Altogether, there were 20 sampling stations, distributed
Sea surface temperature and salinity were obtained from SBE 21 SeaCAT Thermosalinograph every 10 s during both cruises. Surface salinity, in this case, was determined from conductivity salinity using the practical salinity scale (UNESCO, 1985). For the October 2012 cruise, wind speed velocity (wsp) was obtained through the ECMWF portal (European Centre for Medium-Range Weather Forecasts) (http://data-portal.ecmwf.int/), with a spatial resolution of 1.5° latitude by 1.5° longitude. For the September 2014 cruise, wind speed data was collected directly from the meteorological station at the Nho–Cruzeiro do Sul, where wind speed was regularly registered at 30 min intervals.

3.3. Chlorophyll a, nutrients and dissolved organic carbon (DOC)

The chlorophyll a (Chl a) analysis followed the method for determination of Chl a in seawater (Jeffrey and Humphrey, 1975). At each sampling station, surface water (5 L) was collected, filtered and refrigerated on board. The extraction of Chl a was made at the laboratory followed by spectrophotometry analysis (Micronal AJX-6100-PC model).

Absorbance measurements for phosphate and silicate were made using a spectrophotometer (Genesys 2 – Bausch & Lomb) with wave-lengths of 880 nm for phosphate and 810 nm for silicate. The precision of the method is ±0.01 μM for phosphate and ±0.02 μM, for silicate (Grasshoff et al., 1999).

Only for the September 2014 cruise, additional analysis of dissolved organic carbon (DOC) was performed using a HyperTOC Analyzer (THERMOScientific programed with the UV-persulphate (UV_NPOC) oxidation method (THERMO, 2008).

3.4. fCO2 surface seawater and atmosphere measurements.

Both pCO2 underway measuring systems used in the cruises work as described by Pierrot et al. (2009), using air-water equilibrators and an infrared analyzer for CO2 quantification. A continuous flux of surface seawater (approximately 2.5 L min⁻¹) supplied by the vessel’s pump equilibrates with air taken from the top of the vessel (at 10 m high to avoid any contamination from the ship smoke). The gas, free from humidity, passes through a non-dispersive infrared analyzer (LI-COR®, model LI-7000 CO2/H2O gas analyzer) for measurements of CO2 concentrations in the seawater and in the atmosphere.

An electronic device using a LabVIEW 7.0 software controls the pCO2 system. The program recorded and averaged the following parameters every 5 min: date and time, position of the ship, velocity of the ship, molar fraction of CO2 in the equilibrator (xCO2eq), water content in the detector, sea surface temperature (SST) and sea surface salinity (SSS). After every 6 h of seawater molar fraction recording, atmospheric measurements were taken followed by a cycle of standards: air free from CO2 (N2 standard) followed by CO2 standard gases with concentrations of 286.4 ppm, 359.8 ppm and 506.6 ppm (99.9% purity, supplied by White Martins Gases Industriais Ltda.), which were circulated through the system for comparative measurements.

The partial pressure of CO2 in the equilibrator was computed from the molar fraction of CO2 in dry air (xCO2 expressed in ppm) using:

\[ p\text{CO}_2\text{eq} = x\text{CO}_2\text{eq} \cdot (P_{\text{eq}} - P_{\text{w(eq)}}) \]  

(1)

P_eq is the barometric pressure at equilibration (assumed to be the same as the atmospheric pressure at the sea surface) and \( P_{\text{w(eq)}} \) is the water vapor pressure (in atm) calculated at the equilibrator temperature from Weiss and Price (1980). The fugacity of CO2 (in μatm) was calculated as follows (DOE, 1994):

\[ f\text{CO}_2\text{eq} = p\text{CO}_2\text{eq} \cdot \exp(B + 2\delta) \frac{P_{\text{atm}}}{RT} \]

(2)

where \( B = -1636.75 + (12.0408 \; T) - (0.0327957 T^2) +

over five transects, covering an area of approximately 66,000 km² (Fig. 4). This area, extending from the Jaguaribe River to near the São Marcos Bay, represents a larger and wider portion of the Brazilian continental shelf, less oligotrophic and more humid.

A pCO2 underway measuring system was installed on board in both cruises. The first cruise used French equipment, assigned for the bilateral cooperation agreement between France and Brazil. In the second cruise pCO2 measurements were made using a Brazilian prototype, similar to the French system. Other pertinent data (i.e. sea surface temperature, sea surface salinity and wind speed) were collected continuously. Surface seawater samples were collected at each station for chlorophyll a, nutrients and dissolved organic carbon analysis.
(0.0000316528 T³), \( T \) is the equilibrator temperature in Kelvin, \( \delta = 57.7 \)–\( 0.118 T \) and \( R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1} \). A temperature correction, using the formula given by Takahashi et al. (1993), was made to convert the fugacity of CO₂ (in \( \mu \text{atm} \)) in the equilibrator to the fugacity of CO₂ at the sea surface temperature (\( f_{\text{CO}_2}^\text{sw} \)):

\[
f_{\text{CO}_2}^\text{sw} = f_{\text{CO}_2}^\text{eq} \times \exp(0.0423 \times (\text{SST} - T_{\text{eq}}))
\]  

(3)

Fig. 3. Location of sampling stations in the first campaign (October 2012). A dense sampling grid with 12 transects off the continental shelf eastwards Fortaleza covering 57 stations.

Fig. 4. Location of sampling stations in the second campaign, in September 2014. A less dense sampling grid with 5 transects off the continental shelf westwards Fortaleza covering 20 sampling stations.
For ambient air, assuming 100% vapor water saturation, the fugacity of CO2 in the atmosphere ($f_{CO2}^{air}$) was calculated from the molar fraction of atmospheric CO2 ($x_{CO2}^{atm}$):

$$f_{CO2}^{air} = x_{CO2}^{air} \times (P_{atm} - P_{w}(SST)) \times \exp[(B + 2d)P_{atm}/RT]$$ (4)

$Patm$ is the atmospheric pressure and $Pw(SST)$ is the water vapor pressure at the sea surface. The accuracy of the fugacity of CO2 in seawater and in air is estimated at ± 2 μatm.

### 3.5. Calculation of CO2 air-sea flux

The net sea-air CO2 fluxes ($F$, mmol m$^{-2}$ d$^{-1}$) were then calculated using:

$$F = k \cdot K_O \left( f_{CO2w} - f_{CO2air} \right)$$ (5)

where $K_O$ is the solubility of CO2 as a function of SST and SSS (Weiss, 1974) and $k$ is the gas transfer velocity coefficient which was determined previously by many authors (Wanninkhof, 1992; Nightingale et al., 2000; Sweeney et al., 2007; Takahashi et al., 2009). In this study, $k$ was estimated using the recently updated formula in Wanninkhof (2014), which is consistent with wind speed product used. $Sc$ represents the Schmidt number. A positive flux means a source of CO2 to the atmosphere.

$$k = 0.251 \cdot U_{10}^2 \cdot (Sc/660)^{-0.5}$$ (6)

### 3.6. Data processing and statistical analysis

SST, SSS and fCO2 data measured continuously were processed using MATLAB® routines. To obtain the horizontal distribution of state parameters (SST, SSS and fCO2), a grid over the entire sampled area was constructed to facilitate the visualization of the spatial distribution of the surface. The characteristic area of influence of each sample was determined using Voronoi polygons (Aurenhammer and Klein, 1996).

The vertical scale was 1.0 m, which is the resolution of the reduced vertical scale, at the stations near the coast, a difference between the vertical and horizontal scales, at the stations near the coast, a difference between the horizontal and vertical scales, at the stations near the coast, a difference between the horizontal and vertical scales, at the stations near the coast, a difference between the horizontal and vertical scales.

### 3.7. δ13C measures

The carbon isotopic composition of the dissolved organic matter pre concentrated using the Dittmar et al. (2012) procedures was determined, during the second cruise, using an elemental analyzer Flash 2000, with an interface Confo IV, combined to the mass spectrometer Delta V Advantage (Thermo Scientific IRMS). The analytical control was performed by sampling reproductions (triplicates <10%) and certified standards (Elemental Microanalysis Protein Standard) above 95% of precision (Rezende et al., 2010).

### 4. Results

#### 4.1. Physical and biological settings

In the first cruise, $wsp$ ranged from 7.3 to 9.1 m s$^{-1}$ and in the second cruise, from 5.7 to 14.9 m s$^{-1}$. Wind data variation found in the second cruise shows the difference between data collected in situ, with local and temporary wind effects, and data from wind fields from ECMWF, which represent daily means with smoother variations as obtained for the first cruise. André et al. (1986), during the FOCAL cruises, found $wsp$ velocities varying from 4.45 to 6.20 m s$^{-1}$ between 0°–5°S in 35°W also using data from ECMWF reanalysis data sets.

For both cruises, sea surface temperature (SST) and sea surface salinity (SSS) values presented small variations. The mean SST for the first cruise was 26.73 ± 0.14 °C and mean SSS was 36.45 ± 0.24. In the second cruise, in September 2014, the mean SST was 26.8 ± 0.2 °C and mean SSS was 36.1 ± 0.2. For October 2012, SST and SSS presented regions with SST > 27 °C and SSS > 37 near the coast between 36.5°W and 37°W and in regions further away from the coast. We also observed higher salinities near the Jaguari River, where salinities are usually higher than the adjacent continental shelf (S > 39) due to high evaporation rates in relation to rainfall and river damming (Marins et al., 2003). For September 2014, SST distribution was very homogeneous whereas SSS, west of 40°W with values higher than 36 were found. Further east the 40°W there is a big red area stressing SSS values higher than 36 intermixed with lower salinities (SSS < 35.5). Measurements in the tropical Atlantic (5°S–0°) in 1995 found mean SST varying from 28.2 ± 0.2 °C in April to 26.2 ± 0.1 °C in October (Lefèvre et al., 1998).

In the cruise held in October 2012, forty percent (40%) of the hydrographic stations were located within the continental shelf (depth < 70 m) increasing the aspect ratio of the physical processes (ratio between the horizontal and vertical processes). The decrease in depth associated small rainfall and high evaporatranspiration process, semi-arid climate characteristics, increase of the density of tropical water mass (TW) on the continental shelf, whose TS indices are above the isopycnal (σN 24) (Fig. 5a). This behaviour is corroborated in the Fig. 5b, where 98% (98%) of the hydrographic stations are outside of the continental shelf (depth > 70 m), resulting in TS indices below 24 isopycnal ($\sigma$ < 24).

Chlorophyll a (Chl a) concentration in the surface was low during both cruises. The mean Chl a values were 0.09 ± 0.09 μg L$^{-1}$ during October 2012, and 0.12 ± 0.08 μg L$^{-1}$ during the September 2014 cruise. The results obtained during the oceanographic expeditions of REVIZEE...
program for the Brazilian northeast ranged from 0.01 and 2.84 μg L⁻¹ during the dry season (Mafalda et al., 2009).

For both cruises, in general, nutrient concentrations were low. Silicate showed the highest concentrations with a mean of 3.72 ± 2.36 μmol L⁻¹ in the first cruise and 2.92 ± 2.54 μmol L⁻¹ in the second cruise. Phosphate values were also low with mean values of 0.19 ± 0.20 μmol L⁻¹ for the first cruise and 0.21 ± 0.34 μmol L⁻¹ for the second cruise (Table 1).

For September 2014, DOC concentrations ranged between 40 and 67.5 μM, with mean concentration of 53.7 μM. The transect adjacent to the SMB region had the highest mean DOC value of 62.1 μM. Mean DOC concentrations found in the continental shelf adjacent to the Parnaíba and Jaguaribe River were 58.5 μM and 48.3 μM, respectively.

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**Table 1**

<table>
<thead>
<tr>
<th>Cruise</th>
<th>Chl a (μg L⁻¹)</th>
<th>Si-SiO₂⁻ (μmol L⁻¹)</th>
<th>P-PO₄³⁻ (μmol L⁻¹)</th>
<th>DOC (μM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oct 2012</td>
<td>(n = 58)</td>
<td>(n = 58)</td>
<td>(n = 58)</td>
<td>(n = 18)</td>
</tr>
<tr>
<td>Mean</td>
<td>0.09 ± 0.09</td>
<td>2.53 ± 2.57</td>
<td>0.17 ± 020</td>
<td>53.7 ± 8.2</td>
</tr>
<tr>
<td>Min</td>
<td>0.01</td>
<td>0.07</td>
<td>0.03</td>
<td>40</td>
</tr>
<tr>
<td>Max</td>
<td>0.63</td>
<td>11.28</td>
<td>0.92</td>
<td>67.5</td>
</tr>
<tr>
<td>Sep 2014</td>
<td>(n = 20)</td>
<td>(n = 20)</td>
<td>(n = 20)</td>
<td>(n = 18)</td>
</tr>
<tr>
<td>Mean</td>
<td>0.12 ± 0.08</td>
<td>3.72 ± 2.36</td>
<td>0.21 ± 0.34</td>
<td>53.7 ± 8.2</td>
</tr>
<tr>
<td>Min</td>
<td>0.02</td>
<td>0.52</td>
<td>0.02</td>
<td>40</td>
</tr>
<tr>
<td>Max</td>
<td>0.40</td>
<td>9.68</td>
<td>1.15</td>
<td>67.5</td>
</tr>
</tbody>
</table>

**Fig. 5.** Diagram showing the relationship between sea surface temperature and salinity during a) October 2012 and b) September 2014.
DOC levels measured in the Brazilian Northeast continental shelf were lower than the expected for tropical systems (70–80 μmol kg\(^{-1}\)) (Hansell et al., 2009). High fresh water inputs into some regions of the tropical ocean due to the presence of large rivers like the Amazon, Ori-noco and others (Dai et al., 2012) imply in high DOC concentrations, whereas low river inputs to the continental shelf during the dry season (Dias et al., 2013) in the study site leads to low DOC concentrations.

There are no previous measurements of DOC in this region of the Brazilian northeast continental shelf, mean DOC concentrations in the continental shelf adjacent to the SMB and the Parnaíba River were similar to those observed in oligotrophic waters from the Mediterranean Sea, which ranged between 57 and 68 μM (Santinelli et al., 2010). Low concentrations of DOC (56–76 μM) were also recorded in coastal waters of the northern Tyrrhenian Sea during a period of weak flow caused by meteorological conditions (Vignudelli et al., 2004).

However, DOC levels near the Jaguaribe River were even lower, like those estimated by remote sensing in the middle continental shelf of the China Sea (~45 to 60 μM). These low values correspond to the oligotrophic zone of the China Sea caused by upwelling events that brings DOC-poor waters to surface (Pan et al., 2013, Pan and Wong, 2015).

4.2. Distribution of fCO\(_2\) in the surface seawater and the atmosphere

In October 2012, the mean of fCO\(_2\)\(^{air}\) was 400.2 ± 6.0 μatm and fCO\(_2\)\(^{sw}\) was 375.8 ± 2.0 μatm. The lower value of fCO\(_2\)\(^{sw}\) was 388.3 μatm in the regions east of the Jaguaribe River and the highest value reached 413.9 μatm near Fortaleza, in regions west of the Jaguaribe River. In the second cruise, in September 2014, fCO\(_2\)\(^{sw}\) values ranged from 371.9 μatm to 411.7 μatm and the mean value was 391.2 ± 6.4 μatm. The highest values were found near the SMB. The mean fCO\(_2\)\(^{air}\) value was 368.9 ± 2.2 μatm, the maximum fCO\(_2\)\(^{air}\) value found was 371.9 μatm and the minimum fCO\(_2\)\(^{air}\) was 363.6 μatm (Table 2). These fCO\(_2\)\(^{sw}\) values are in the same range of recently reported values for the west equatorial Atlantic Ocean (Ibañez et al., 2016; Lefèvre et al., 2014). The fCO\(_2\)\(^{sw}\) values of the entire surveyed area were lower than the fCO\(_2\)\(^{sw}\) but still very close, with ΔCO\(_2\) ranging from +12.5 to +61.6 μatm in the first cruise and +4.1 to +48.2 μatm in the second cruise. The fCO\(_2\)\(^{sw}\) distributions for the different sampling periods are shown in Fig. 6.

4.3. Statistics

A Spearman correlation matrix of fCO\(_2\) distribution along the study area with seawater properties such as SST, SSS, wsp, nutrients and Chl \(a\) for the first cruise is presented in Table 3a. DOC was included for the cruise of September 2014 in Table 3b.

For October 2012, the only significant correlation found was between fCO\(_2\)\(^{sw}\) and SSS while the other variables showed no significant correlation with fCO\(_2\)\(^{sw}\), corroborating with Dias et al. (2013) observations of oceanic intrusion. In this portion of the continental shelf, during this season, we can infer that the SSS is the parameter that most influences the variability of the fCO\(_2\)\(^{sw}\) and that this region has a similar behaviour to the open ocean waters, probably being controlled by physical parameters throughout the year.

However, for the September 2014, with broadening of the study area, reaching receptors of larger rivers in the westernmost part of the continental shelf than the area covered in 2012, it was found significant positive correlations between fCO\(_2\)\(^{sw}\) and physical parameters such as: SST, SSS, wsp but also with Chl \(a\) and silicate (Si-SiO\(_2\)) and a negative correlation with phosphate (P-PO\(_4\)) appears (Table 3b).

This suggests that, despite the low values measured for both Chl \(a\) and nutrients, they seem to influence the CO\(_2\) processes in a larger portion of the coast. Probably showing differences between ocean and continental influences from the eastern to the western equatorial coast, with the predominance of ocean forcing at the east.

Phosphorus is absorbed by phytoplankton in the sea surface and together with Nitrogen are limiting nutrients for the photosynthetic activity (Downing, 1997). With the increase of Chl \(a\), a decrease in fCO\(_2\) was expected. There was no significant correlation between fCO\(_2\) and DOC.

The cluster analysis revealed two distinct groups A and B (Fig. 7). Group A containing only October 2012 stations (Stations starting with ‘O’ are related to the first cruise) and Group B containing September 2014 stations (Stations starting with ‘S’ are for stations of the second cruise) and stations of the first cruise (O23 O24 O26 O27) which belong to the same transect (transect 6). It was observed that the subgroups formed separated stations located in the eastern regions from stations in western regions. In general, the stations of the same transect belonged to the same group, showing homogeneity along the transect and the heterogeneity observed was longitudinal, between east and west, reinforcing the hypothesis of transition between two different behaviour areas as we moved to the west.

For October 2012, it was observed no variation between the inner and external continental shelf, showing that during the dry season, the continental influence was not enough to be found off in the ocean. The longitudinal variations (west to east) are more evident. For September 2014, stations of transects 1 and 2 were grouped in subgroup B1 together with October stations from transect 6, and transects 3, 4, 5 and formed a subgroup B2. This separation is probably marking the transition between distinct behaviour areas, as it was observed that highest fCO\(_2\) values were found in stations 3, 4 and 5 compared with lowest fCO\(_2\) values of transects 1 and 2.

In addition to the relationships between CO\(_2\) and physical and chemical parameters, the influence of the continental contribution can be observed by the \(δ^{13}C\) distribution in the dissolved organic matter, along the study area where lighter \(δ^{13}C\) values predominated in the portions of the continental shelf under stronger influence of river discharges (Fig. 8) (Mangrove: \(δ^{13}C\) −27.9 ± 1.4‰, Phyttoplankton: \(δ^{13}C\) −21.0 ± 0.8‰) (Fry et al., 1998; Kuramoto and Minagawa, 2001; Rezende et al., 2010). Also of notice is the existence of the world largest continuous mangrove forest bordering the western portion of the studied area. This forest is a significant carbon source to the continental shelf in the region (Lacerda et al., 2001).

4.4. Air-sea CO\(_2\) flux in the Brazilian equatorial northeast coast

The air-sea flux obtained by calculation was positive for both cruises, indicating that the region works as a source of CO\(_2\) for the measured periods, as a consequence of the tropical Atlantic high fCO\(_2\) values.

The average CO\(_2\) fluxes for the first cruise period was +3.28 ± 1.07 mmol m\(^{-2}\) d\(^{-1}\). The maximum flux value reached +7.24 mmol m\(^{-2}\) d\(^{-1}\) and occurred in the transect nearby Fortaleza. The lowest flux value was +1.66 mmol m\(^{-2}\) d\(^{-1}\).

The estimated flux for September 2014 was also positive throughout the course of the cruise and the mean value was 5.87 ± 3.06 mmol m\(^{-2}\) d\(^{-1}\). The flux values reached a maximum of 14.62 mmol m\(^{-2}\) d\(^{-1}\) in 41°W and a minimum value of 0.89 mmol m\(^{-2}\) d\(^{-1}\) in 37°W.
Andrié et al. (1986) found global mean net CO₂ flux from the ocean to the atmosphere of 1.05 mmol m⁻² d⁻¹ between 5°N and 5°S. They also found that the release of CO₂ increases from east to west. Lefèvre et al. (2014) calculated the mean CO₂ fluxes for March 2009 and July 2010 and found the area south of 2.5°S as a strong source of CO₂ with fluxes > 3 mmol m⁻² d⁻¹.

Plotting the CO₂ flux values of the two cruises together, the values obtained for the first cruise are in the same range as those obtained in Fig. 6.


Table 3a
Spearman’s rank correlation coefficients for variables of the October 2012 cruise (n = 27).

<table>
<thead>
<tr>
<th>CO₂ (atm)</th>
<th>SST</th>
<th>SSS</th>
<th>Wsp</th>
<th>Chl a</th>
<th>Si-SiO₂</th>
<th>P-PO₄⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ (atm)</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SST</td>
<td>0.26</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SSS</td>
<td>-0.62*</td>
<td>-0.40*</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wsp</td>
<td>0.32</td>
<td>0.29</td>
<td>-0.46</td>
<td>1</td>
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<td></td>
</tr>
<tr>
<td>Chl a</td>
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<td>-0.19</td>
<td>0.24</td>
<td>-0.32</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.26</td>
<td>0.21</td>
<td>-0.05</td>
<td>-0.02</td>
<td>0.01*</td>
<td>1</td>
</tr>
<tr>
<td>P-PO₄⁻</td>
<td>0.10</td>
<td>0.20</td>
<td>-0.23</td>
<td>0.34</td>
<td>-0.16</td>
<td>0.37*</td>
</tr>
</tbody>
</table>

* Marked correlations are significant at p < 0.05.

Table 3b
Spearman’s rank correlation coefficients for variables of the cruise of September 2014 (n = 15).

<table>
<thead>
<tr>
<th>CO₂ (atm)</th>
<th>SST</th>
<th>SSS</th>
<th>Wsp</th>
<th>Chl a</th>
<th>Si-SiO₂</th>
<th>P-PO₄⁻</th>
<th>DOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ (atm)</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SST</td>
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<td>1</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>SSS</td>
<td>0.53*</td>
<td>0.15</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wsp</td>
<td>0.61*</td>
<td>0.16</td>
<td>0.74*</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chl a</td>
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<td>0.16</td>
<td>0.58*</td>
<td>0.60*</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.32*</td>
<td>0.24</td>
<td>0.28</td>
<td>0.37</td>
<td>0.28</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>P-PO₄⁻</td>
<td>-0.75*</td>
<td>-0.63</td>
<td>-0.41</td>
<td>-0.60*</td>
<td>-0.40</td>
<td>-0.35</td>
<td>1</td>
</tr>
<tr>
<td>DOC</td>
<td>0.39</td>
<td>0.52*</td>
<td>0.56*</td>
<td>0.41</td>
<td>0.53*</td>
<td>-0.04</td>
<td>-0.70*</td>
</tr>
</tbody>
</table>

* Marked correlations are significant at p < 0.05.
the same longitudes during the second cruise (Fig. 9), showing good agreement between data in the same region and in the same season. Studies assessing the variations of this source over time have led to different conclusions (Andrié et al., 1986; Oudot et al., 1995), there is no consensus over this subject yet. Local increase or decrease of fCO2 can be induced by vortices and may be associated with current circulation. More data need to be evaluated to better detect CO2 trends in the Tropical Atlantic (Lefèvre et al., 2014).

5. Discussion

This study presents fCO2sw, fCO2air and CO2 fluxes for an under sampled region of the Brazilian Northeast continental shelf. Despite the small variability expected for this region, a transition of behaviour was revealed between east and west. This highlights the importance of coastal zones measurements as they can present such a different behaviour when compared to global ocean areas.

For the cruise of October 2012, a condition of limited continental influence, during the sampled period, with the predominance of the intrusion of oceanic water in the continental shelf seems to be dominant during that cruise. The origin of CO2 in this region, in the dry season, probably comes from tropical oceanic waters super-saturated with CO2 instead of continental contributions. A strong oligotrophic condition is predominant and the primary production is very low in this region during this time of the year. The influence of the terrestrial fluxes of organic matter to the oceans through rivers, observed in many regions of the world (Ludwig et al., 1996), do not occurred here where the rivers’ influence depends on an expressive rainy season that does not always occur.

Dias et al. (2013), during an extreme period of maximum river discharge of the Jaguaribe River measured a 6 km long estuarine plume, whose influence extends only to the inner continental shelf and restricted to a 2 meters depth layer at the surface. This indicates that the intrusion of tropical water on the continental shelf is stronger than the continental influence, even when it does exist.

However, in October 2012, the fCO2sw showed minimum values near the Jaguaribe River contribution. This suggests that only during a strong rainy season, this river may transport nutrients enough to enhance primary production and change the CO2 behaviour locally.

In September 2014, the minimum values of fCO2sw occurred also in the continental shelf adjacent to the Jaguaribe and Parnaíba River contributions. This leads to the hypothesis that after severe rainy season, stronger river discharges with more nutrients reaching the coast together with good light penetration, primary production would be enhanced and CO2 could be absorbed. The fCO2sw values increased westwards showing maximum values adjacent to the São Marcos Bay. At the SMB, high turbidity and action of macrotides (>6 m) are the main causes of the small thickness of the photic zone due to rapid attenuation of light energy, thus causing reduction in absorption of light by phytoplankton and thus reducing photosynthesis (Azevedo et al., 2008). These characteristics combined with higher SSS (>36) measured during the cruise near the influence of SMB may favor the increase of fCO2.

Fig. 8. δ13C distribution in the dissolved organic matter sampled during the September 2014 cruise.
5.1. \( \text{fCO}_2 \) measurements in the tropical Atlantic

High \( \text{fCO}_2^{\text{sw}} \) values were measured in other studies in the Tropical Atlantic usually characterizing it as a source of \( \text{CO}_2 \) to the atmosphere (Andrié et al., 1986; Goyet et al., 1998; Lefèvre et al., 2013). FOCAL Cruises 2, 4, 6 and 8 between 0 and 5°S along 35°W found \( \text{pCO}_2^{\text{sw}} \) between 365 and 408 µatm. Goyet et al. (1998) measurements in the Tropical Atlantic Ocean between 7°30′N and 32°S along 19°W during WOCE A15 found \( \text{pCO}_2^{\text{sw}} \) results resembling those found during FOCAL cruises but an increase of 10 µatm in \( \text{pCO}_2^{\text{sw}} \), indicating a decrease on \( \text{CO}_2 \) supply to the atmosphere. Further measurements made in the Tropical Atlantic (20°N–20°S) attributed the supersaturation to the \( \text{CO}_2 \) supplied from equatorial and coastal upwelling (Lefèvre et al., 1998).

Surface seawater \( \text{CO}_2 \) concentrations below atmospheric levels due to the influence exerted by the Amazon River discharge, close to the 55° W, were verified by Körtzinger (2003), Lefèvre et al. (2010) and Ternon et al. (2000), but the region sampled in our cruise is not close enough to receive such influence. However, a decrease in \( \Delta \text{CO}_2 \) was evidenced in the second cruise, which reached a transition area where climatic conditions starts to change to humid in comparison with the first one where semi-arid climate domains.

5.2. Factors controlling seawater \( \text{CO}_2 \) fugacity

Temperature increase tends to enhance \( \text{fCO}_2 \), whereas biological activity is also an important factor on \( \text{fCO}_2 \) control, mainly over the coast. Based in the statistical analysis, SST was the most significantly driver of \( \text{fCO}_2^{\text{sw}} \) variation. We believe that with more frequent measurements in the region over an annual cycle, it will be possible to improve the SST–\( \text{fCO}_2^{\text{sw}} \) relation for the construction of a strong regional algorithm allowing future \( \text{fCO}_2^{\text{sw}} \) predictions to be applied to this part of the Brazilian coast.

6. Conclusion

This study represents the first screening of the distribution of the \( \text{fCO}_2 \) in the surface waters of the continental shelf off the Brazilian Equatorial Northeastern coast. Data on \( \text{fCO}_2^{\text{sw}} \) indicate that the area is supersaturated with respect to the overlying marine air causing a net \( \text{CO}_2 \) release to the atmosphere.

CO\(_2\) annual performance needs to be improved with higher sampling frequency along the years so that we can better understand the \( \text{CO}_2 \) seasonal variations. Different characterization of the eastern and the western portion of the Northeast continental shelf showed different behaviours. The eastern part of the shelf works similarly to the open ocean regarding \( \text{fCO}_2 \) influenced by physical parameters, mostly SSS, whereas the western part of the shelf seems to have a more complex behaviour influenced by physical parameters such as SST, SSS and wsp but also by nutrients and Chlorophyll \( a \). Even with small concentrations, Chl \( a \) and nutrients seem to have a significant importance on \( \text{fCO}_2^{\text{sw}} \) distribution on this continental margin.

Anthropogenic impacts to the coastal and estuarine waters tend to increase, with the growth of aquaculture activities and river damming in these regions, this pressure will probably affect the \( \text{CO}_2 \) behaviour. Generally, global models do not represent these areas well enough, enhancing the need for \( \text{pCO}_2 \) measurements and associated air-sea \( \text{CO}_2 \) fluxes in the continental margins. This work represents the first steps in the study of the coastal region in relation to \( \text{CO}_2 \) behaviour in this study area. In the last cruise, a Brazilian \( \text{CO}_2 \) device, constructed by an innovative technological independence effort, was used, contributing to enhance the number of field measurements of the partial pressure of \( \text{CO}_2 \) in the country’s continental margins. We hope that an increase in the number of \( \text{pCO}_2 \) measurements in the continental margins can contribute to future calibration of regional and global models.

Acknowledgments

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