Edaphic factors controlling summer (rainy season) greenhouse gas emissions (CO_2 and CH_4) from semiarid mangrove soils (NE-Brazil)

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HIGHLIGHTS

- GHG emission was associated with different soil characteristics.
- Highest CO_2 emissions were found in mangroves with larger dissolved C and lower DOP.
- Less CH_4 flux was due to low DOP in semiarid mangrove soils.

GRAPHICAL ABSTRACT
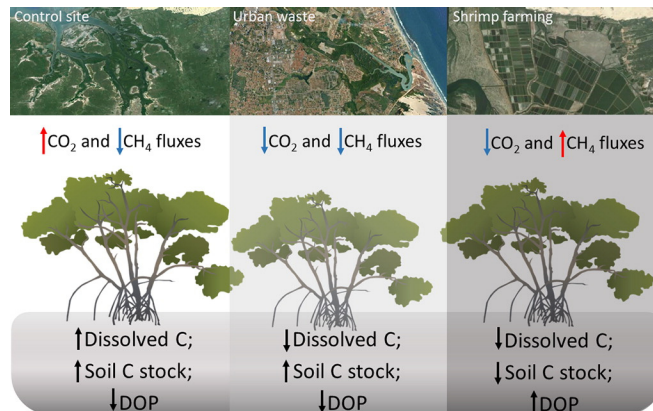
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ABSTRACT

The soil attributes controlling the CO_2, and CH_4 emissions were assessed in semiarid mangrove soils (NE-Brazil) under different anthropogenic activities. Soil samples were collected from different mangroves under different anthropogenic impacts, e.g., shrimp farming (Jaguaribe River); urban wastes (Cocó River) and a control site (Timonha River). The sites were characterized according to the sand content; physicochemical parameters (Eh and pH); total organic C; soil C stock (SCS) and equivalent SCS (SCS_{EQV}); total P and N; dissolved organic C (DOC); and the degree of pyritization (DOP). The CO_2 and CH_4 fluxes from the soils were assessed using static closed chambers. Higher DOC and SCS and the lowest DOP promote greater CO_2 emission. The CH_4 flux was only observed at Jaguaribe which presented higher DOP, compared to that found in mangroves from humid tropical climates. Semiarid mangrove soils cannot be characterized as important greenhouse gas sources, compared to humid tropical mangroves.

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1. Introduction

Mangroves are tropical and subtropical coastal ecosystems characterized by their high productivity (Komiyama et al., 2008) and their capacity to store large amounts of organic C in its soils (Donato et al., 2011; Nellemann et al., 2009). The C accumulation in its soils is a function between the inputs of organic C compounds, formed basically by photosynthetic processes sequestering atmospheric CO_2, and the losses caused by decomposition, erosion and leaching (Neue et al., 1997; Stockmann et al., 2013). The organic compounds enter the edaphic system as litter, decaying roots, root exudates, and microbial biomass, which are decomposed by the activity of micro- and mesofauna (Oades, 1998).

In mangroves, due to the frequent flooding event by seawater, organic matter decomposition occurs by reducing other electron acceptors substituting the O_2 (i.e., $O_2 \rightarrow NO_3^- \rightarrow Mn$ oxyhydroxides $\rightarrow Fe$ oxyhydroxides $\rightarrow SO_4^{2-} \rightarrow CO_2$), decreasing the decomposition rate as a result of the lower energetic yield (Alongi et al., 2001; Howarth, 1984; Neue et al., 1997; Reddy et al., 1986). Because of the combination of high biomass production and low decomposition rates, mangroves, and other coastal wetlands have been denominated as "Blue Carbon sinks" emphasizing the important role that these ecosystems perform in sequestering atmospheric CO_2 (Duarte et al., 2005; Mcleod et al., 2011; Nellemann et al., 2009; Howard et al., 2014).

Despite its ecological importance, including its role in sequestering atmospheric CO_2, the mangrove forests are declining to extinction due to anthropogenic impacts that directly remove the vegetation, e.g., aquaculture, urbanization and coastal landfill (Duke et al., 2007). Globally, the mangroves occupy 0.7% of the tropical forest area, but their destruction currently adds 10% to global CO_2 release from tropical deforestations (Alongi and Mukhopadhyay, 2015).

Other activities (i.e., shrimp farming and eutrophication) are related to nutrient-rich effluent release, which promotes changes in the soil characteristics and stimulates organic matter decomposition, increasing CO_2 fluxes (Aschenbroich et al., 2015; Chen et al., 2010; Suarez-Abelenda et al., 2014). In addition, mangroves can be an important source of CH_4 and N_2O to the atmosphere (Barnes et al., 2006; Kristensen et al., 2008b; Purvaja and Ramesh, 2001) contributing to global climatic changes due to its warming potential (Lashof and Ahuja, 1990; Chauhan et al., 2015).

CO_2 production in mangrove soils refers to microbial activity during organic matter degradation, mainly, and root respiration (Chen et al., 2012; Lovelock et al., 2011). The CO_2 flux to the atmosphere occurs when microorganisms oxidize the organic C using O_2, NO^{3-}, Mn^{4+}, Fe^{3+}, and SO_4^{2-} as electron acceptors. On the other hand, CH_4 production occurs in flooded areas using CO_2 or other methyl compounds under extreme anoxic conditions ($Eh < -150$ mV; Chen et al., 2010; Kristensen et al., 2008a, 2008b; Yu et al., 2006). Besides, N_2O is produced by nitrification processes, converting ammonium to nitrate under aerobic conditions or by a denitrification process that involves anaerobic reduction of nitrate to N_2 (Conrad, 1995; Chauhan et al., 2015). Since the GHG emission is performed through microbial processes, the edaphic and climatic factors (e.g., redox potential; organic C content; salinity and temperature) may affect these emissions (Chen et al., 2010, 2011, 2012; Livesley and Andrusiak, 2012).

This study aimed to evaluate edaphic factors influencing greenhouse gas (CO_2 and CH_4) emissions from semiarid mangrove soils (NE-Brazil) under different anthropogenic activities, in order to better comprehend the role of these endangered ecosystems for GHG emissions and C sequestration, based on the hypothesis that: 1) lower redox potential and higher degree of iron pyritization can enhance methane emission whereas higher redox potential and lower degree of pyritization promote higher CO_2; and 2) the mangrove soils with greater soil carbon stock present lower CO_2 emission.

2. Material and methods

2.1. Study site

The study site is located at the Brazilian semiarid coast (Ceará state, NE-Brazil; Fig. 1), which is characterized by two distinct seasons: an extended dry period (rainfall <200 mm; from June to January) and a rainy season (from February to May; approximately 1000 mm rainfall), but with a small variation in the daily mean temperature (from 25 to 29 °C; Fig. 1; IPECE, 2010; Sales, 2008; Silva and Souza, 2006). The coastal zone of the Ceará is characterized by a small river discharge into the estuaries, which results in higher salinity and a decrease in the development of mangrove forests (Maia et al., 2006; Schaeffer-Novelli et al., 1990).

The samples were collected from 3 mangroves under different anthropogenic impacts: the Cocó River is mostly affected by urban wastes and deforestation; the Jaguaribe River receives effluent discharge from shrimp farming ponds; whereas the Timonha River is far west of the state, where anthropic influences are minimal, and considered an undisturbed mangrove (Fig. 1; Silva and Souza, 2006; Nóbrega et al., 2015).

2.2. Soil sampling procedure and physicochemical (Eh and pH) characterization

The soil samples were collected during the rainy period (April 2012) in mangrove forests predominantly vegetated by *Rhizophora* spp. We collected nine undisturbed soil samples using PVC tubes attached to a soil sampler for flooded soils in each mangrove. The samples were hermetically sealed and transported in a vertical position at approximately 4 °C. In the laboratory, six of the soil samples (collected with the PVC tubes) were cut at intervals of 10 cm until a depth of 40 cm (0–10; 10–20; 20–30 and 30–40 cm), accounting for 24 samples from each estuary. Sub-samples were dried (105 °C) and sieved (2 mm mesh), whereas other sub-samples were frozen for posterior analysis. The other three undisturbed samples were used to obtain the soil bulk density (ρ = mass of the soil solids / total soil volume) for the soil carbon stock (SCS) calculation.

The redox potential (Eh) and pH were measured in the field after equilibrating the electrodes with the samples collected using a semi-opened cylinder soil sampler. The Eh was measured using a platinum electrode and the final readings were corrected adding the potential of the calomel reference electrode (+244 mV). The pH values were obtained used a glass electrode previously calibrated with pH 4.0 and 7.0 standard solutions.

2.3. Soil characterization

The soils from each sampling site were characterized regarding the content of sand, total contents of organic carbon (TOC), nitrogen (TN), sulfur (TS) and phosphorous (TP), dissolved organic carbon (DOC), reactive iron ($Fe_{REACTIVE}$) and pyritic iron (Fe_{PYRITE}). Also, the degree of Fe pyritization (DOP), the soil C stock (SCS) and the equivalent soil C stock (SCS_{EQV}) was calculated.

The sand content was quantified by sieving the sample in a 50 μm mesh after the oxidation of the soil organic matter (using H_2O_2, 30%) and chemical dispersion (0.015 M $(NaPO_3)_6$ + 1.0 M NaOH; Gee and Bauder, 1986). The TOC and TN contents were obtained by an elemental analyzer (LECO 144 SE-DR). For TOC quantification, subsamples were pretreated using HCl to remove the inorganic C while the TN quantification was performed using untreated samples (Byers et al., 1978; Schulte, 1995). The TP was extracted with nitric acid boiling the samples for 3 h (130 °C, approximately) and calorimetrically quantified using the molybdenum blue method (Pansu and Gautheyrou, 2006). The dissolved organic carbon (DOC) was calorimetrically quantified (Bartlett
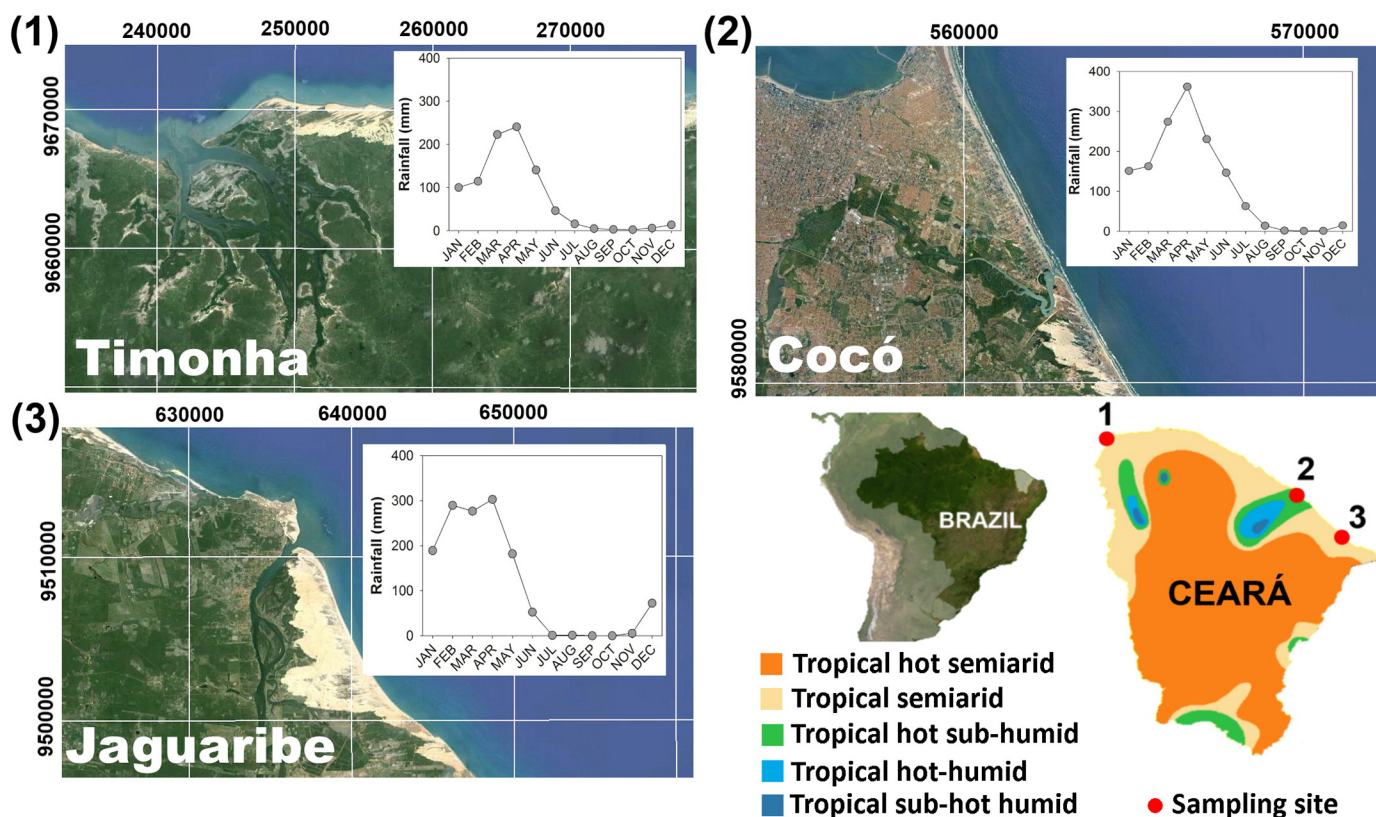
Fig. 1. Sampling site location and climatic classification for the three studied mangroves (1 — Timonha River, control site; 2 — Cocó River, affected by urban wastes and 3 — Jaguaribe River, affected by shrimp farming).

and Ross, 1988) in interstitial water samples, obtained by centrifugation (6000 rpm for 30 min).

The quantification of $Fe_{REACTIVE}$ and Fe_{PYRITE} was performed using frozen samples according to the sequential extraction method proposed by Huerta-Diaz and Morse (1990, 1992). Initially, $Fe_{REACTIVE}$ was extracted with a 1 M HCl solution (16 h agitation), followed by pre-treatment to remove Fe associated with silicates (HF 10 M) and organic matter (H_2SO_4). Afterward, the Fe_{PYRITE} was extracted using concentrated nitric acid (2 h agitation). Thus, the degree of pyritization (DOP) was calculated according to Berner (1970) (DOP (%) = Fe_{PYRITE} / ($Fe_{REACTIVE}$ + Fe_{PYRITE}).

The soil carbon stock (SCS) was quantified to a 40 cm depth using ρ and the TOC content (SCS = TOC × ρ × 40 cm; Mckenzie et al., 2000) for the 3 estuaries. To compare the soil carbon stock for the same soil masses, equivalent soil depths were calculated for the disturbed estuaries using $\rho_{TIMONHA}$ as a reference soil bulk density (Ellert and Bettany, 1995). The equivalent depth was calculated as $Z_{EQV} = (\rho_{TIMONHA} / \rho_{DISTURBEDESTUARY})$ and, thus, the corrected SCS was calculated as $SCS_{EQV} = TOC \times \rho_{DISTURBEDESTUARY} \times Z_{EQV}$. The use of an equivalent depth for soil carbon stock calculations can be useful when comparing ecosystems with different values of soil bulk density, when higher stock values are related to more dense soils (e.g., due to grain size composition, compaction, subsidence) instead to higher organic carbon content (Ellert and Bettany, 1995).

2.4. GHG sampling and analysis

In each sampling site, three static chambers were used for carbon gas (CO_2 and CH_4) collection. The rigid chambers (17.5 cm diameter and 17.5 cm height, inserted 5 cm into the soil) presented a low volume/basal area ratio for rapid gas concentration, but large enough to minimize surface effects. The samples were collected using nylon syringes (BD type) attached to the top of the chamber after a short stabilization time. Gas samples were taken using pre-established intervals (0, 10, 20, 30 min), at the same time, measuring the air and soil temperature and air humidity. The samples were sent to the laboratory where the gas concentrations were measured by gas chromatography (Varian Inc., Palo Alto, CA). The GHG flux (g m^{-2} h^{-1}) was calculated using the gas concentration, air temperature, chamber volume, basal area (area of soil inside the chamber), and atmospheric pressure (Howard et al., 2014). The changes in the concentration over the time in the closed chamber, with a measured volume, reflect the gas emission from the basal area (also known). Thus, the mass of GHG in each time interval is calculated using the universal gas equation (PV = nRT), obtaining an equation for mass flux (g h^{-1}) for each chamber. And then the mass flux isdivided by basal to express the emission on a per area basis (g m^{-2} h^{-1}; for further details, please see Howard et al., 2014).

2.5. Statistical analysis

To compare the results obtained in each mangrove, the average values were evaluated by one-way ANOVA and compared by the posthoc Tukey test with a 5% minimum significance value.

3. Results

3.1. Characterization of the sampling sites

The results indicate a marked difference between the areas studied. The lower Eh values were found in the mangrove from Jaguaribe River (average of all the depths: -87 ± 76 mV), followed by Timonha (average: $+93 \pm 107$ mV) and Cocó (average: $+168 \pm 94$ mV). In all three sites, the Eh values were lower at deeper layers (Fig. 2A). On the other hand, higher pH values were found in samples from Jaguaribe
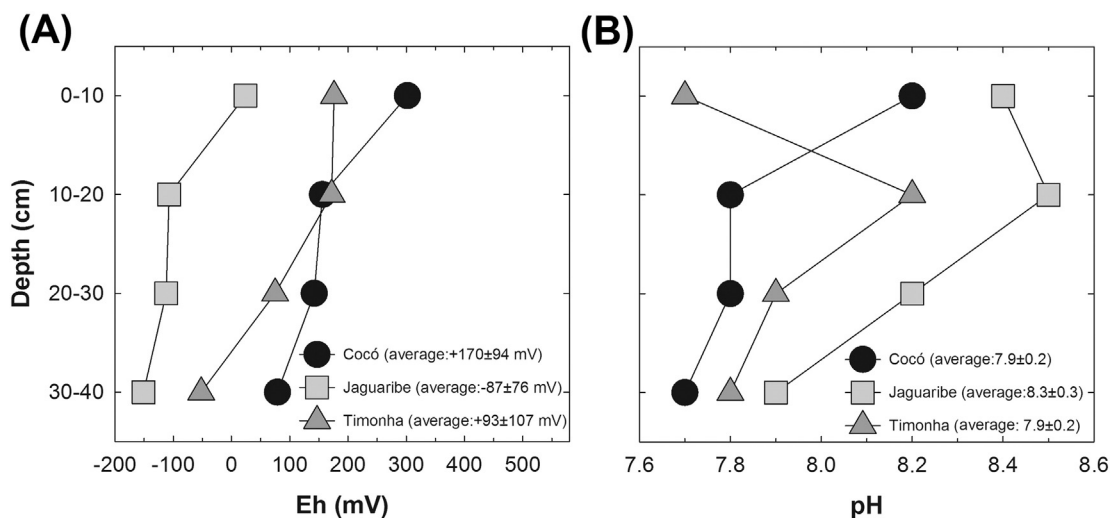
Fig. 2. Physico-chemical characterization: Eh (A) and pH (B) for the three studied mangroves (Timonha River, control site; Cocó River, affected by urban wastes; and Jaguaribe River, affected by shrimp farming).

River (average: 8.3 ± 0.3), while the samples from Timonha and Cocó River presented the same pH average (average: 7.9 ± 0.2; Fig. 2B).

Regarding the sand contents, the studied sites presented a wide variation in the grain size composition with sand content ranging between 2.7% and 75.8%. The lower sand contents were found in the samples from Jaguaribe River (average: 3.4 ± 1.0), whereas higher were found in the Cocó River mangrove (average: 62.4 ± 11.9%). In the Timonha River, the sand content ranged between 39.4 and 56.3%, with an average of 48.2 ± 7.4% (Fig. 3).

Comparing the TOC contents, the measured values presented significant differences ($P < 0.005$) among the three studied mangroves, with higher values found at Jaguaribe River (average value for all depths: 46.8 ± 10.8 g kg^{-1}) followed by Timonha (average: 37.0 ± 2.8 g kg^{-1}) and Cocó (average: 25.7 ± 9.4 g kg^{-1}; Fig. 4A). Similarly, higher TP content ($P < 0.005$) was measured in the Jaguaribe River (average: 0.33 ± 0.05 g kg^{-1}; Fig. 4B), followed by Timonha (average: 0.17 ± 0.01 g kg^{-1}). The TN content ranged from 3.0 ± 0.2 g kg^{-1} (Jaguaribe River, 0–10 cm) to 0.6 ± 0.1 g kg^{-1} (Timonha, 0–10 and 30–40 cm). The significantly higher ($P < 0.005$) TN values were found in Jaguaribe (average for all depths: 2.4 ± 0.5 g kg^{-1}; Fig. 4C), followed by Cocó (average for all depths: 1.1 ± 0.5 g kg^{-1}) and Timonha (0.7 ± 0.1 g kg^{-1}).

The dissolved organic carbon (DOC) concentrations were significantly higher ($P < 0.005$) at the Timonha mangrove (average of all depths 9.0 ± 0.6 mmol l^{-1}), when compared to Jaguaribe (average of

all depths 7.9 ± 1.3 mmol l^{-1}) and Cocó (average of all depths 7.9 ± 0.3 mmol l^{-1}; Fig. 4D), which did not presented significant difference.

The Fe$_{REACTIVE}$ contents varied between 21.0 ± 2.9 mmol kg^{-1} and 72.5 ± 6.3 mmol kg^{-1} (Fig. 4E). Significative ($P < 0.005$) highest Fe$_{REACTIVE}$ values were found in the Jaguaribe mangrove (average for all depths equal to 70.7 ± 14.8 mmol kg^{-1}), compared to the values from the Cocó and Timonha (average for all depths: 26.4 ± 11.9 and 23.0 ± 3.4 mmol kg^{-1}, respectively; Fig. 4E). Similarly, the Fe$_{PYRITE}$ contents varied widely within the samples (from 24.5 ± 5.4 to 286.0 ± 48.7 mmol kg^{-1}), with significantly higher values ($P < 0.005$) in the samples from Jaguaribe River (average for all depths: 76.4 kg ± 202.5 mmol kg^{-1}; Fig. 4F), followed by Cocó River (average for all depths: 55.9 ± 23.7 mmol kg^{-1}) and Timonha (average for all depths: 34.8 ± 11.8 mmol kg^{-1}). Despite the wide variation in the Fe$_{PYRITE}$, the DOP values showed a smaller variation, with values ranging from 56.0 ± 4.8 to 78.5 ± 3.9%. The higher DOP values were found in Jaguaribe (72.2 ± 9.5%), followed by Cocó (67.7 ± 8.7%) and Timonha Rivers (58.1 ± 13.4%; Fig. 4G).

A significantly higher ($P < 0.005$) ρ value was found in the Timonha River mangrove ($\rho_{TIMONHA}$; mean value: 1.01 ± 0.06 g cm^{-3}), whereas the lowest value was measured for the Jaguaribe mangrove soil ($\rho_{JAGUARIBE}$; mean of 0.45 ± 0.02 g cm^{-3}) and the for the Cocó River ($\rho_{COCÓ}$) it was equal to 0.81 ± 0.04 g cm^{-3}. The higher soil carbon stock ($P < 0.005$) was calculated for the Timonha River (14.8 ± 1.1 kg m^{-2}), while the C stocks for the Cocó and Jaguaribe Rivers
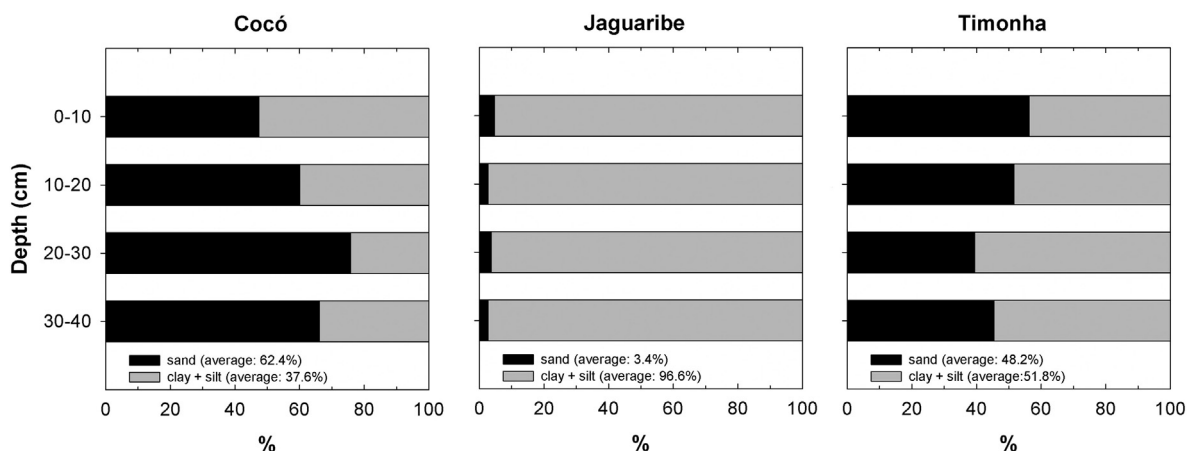
Fig. 3. Sand and silt + clay contents for the three mangroves (Timonha River, control site; Cocó River, affected by urban wastes; and Jaguaribe River, affected by shrimp farming).
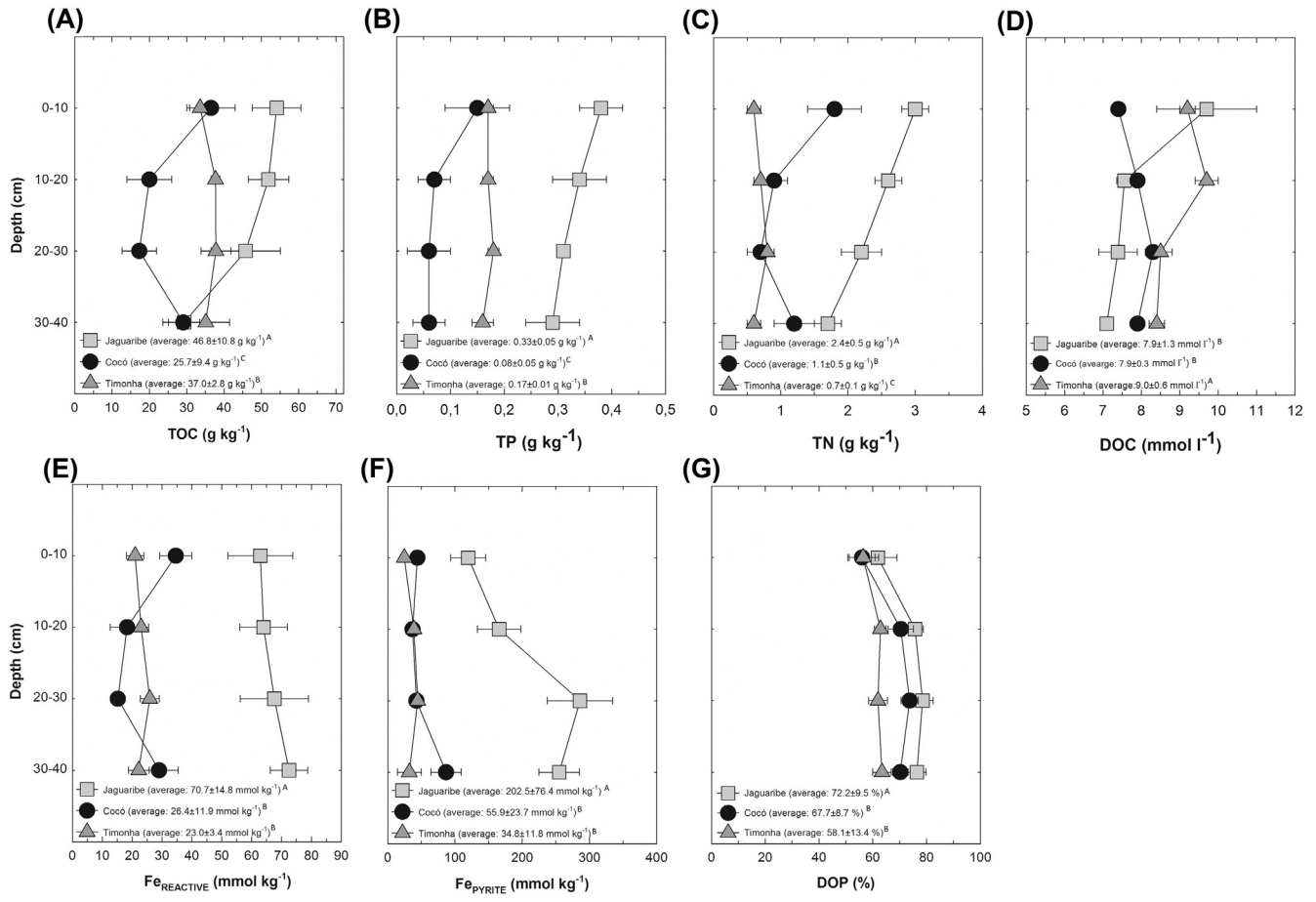
Fig. 4. Contents of total organic carbon (TOC; A), total phosphorus (TP; B), total nitrogen (TN; C), dissolved organic carbon (DOC; D), reactive and pyritic Fe (Fe$_{REACTIVE}$ and Fe$_{PYRITE}$; E and F, respectively) and degree of pyritization (DOP) for the three mangroves (Timonha River, control site; Cocó River, affected by urban wastes; and Jaguaribe River, affected by shrimp farming). The average values followed by different capital letters present significative different values (P < 0.005).

were 8.3 ± 3.0 kg m^{-2} and 8.3 ± 1.9 kg m^{-2}, respectively (Fig. 5A). When the SCS was calculated for the same soil mass (SCS$_{EQV}$), the value accounted for the Jaguaribe soils was 17.8 ± 4.3 kg m^{-2} and 10.3 ± 3.8 kg m^{-2} for the Cocó soils (Fig. 5A).

3.2. CO$_2$ and CH$_4$ fluxes

The significantly higher (P < 0.005) CO$_2$ flux was observed in the Timonha River mangrove (44.4 ± 2.2 mg m^{-2} h^{-1}; Fig. 5B), followed by Jaguaribe (20.5 ± 1.1 mg m^{-2} h^{-1}) and Cocó (16.4 ± 3.8 mg m^{-2} h^{-1}). The highest (P < 0.005) methane flux was recorded

for the Jaguaribe River (8.8 ± 13.8 µg m^{-2} h^{-1}), followed by Timonha (1.3 ± 3.3 µg m^{-2} h^{-1}) and Cocó (Cocó: 0.7 ± 0.5 µg m^{-2} h^{-1}).

4. Discussion

The TOC, TN and TP contents of this study emphasize the great ability of mangrove soils to accumulate carbon and nutrients (Bosire et al., 2008; Bouillon et al., 2003; Donato et al., 2011; Duarte et al., 2005; Gonneea et al., 2004; Khan et al., 2006; Kristensen et al., 2008a; Nellemann et al., 2009). Due to the frequent flooding to which these soils are subject, the microbial respiration occurs by anaerobic pathways, mainly by reducing Fe^{3+} compounds and sulfate (Alongi et al.,
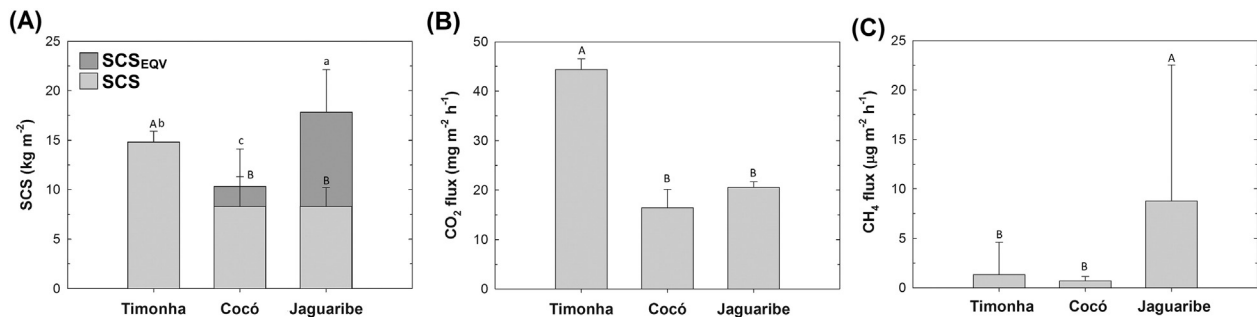
Fig. 5. Soil carbon stock (A) CO$_2$ (B) and CH$_4$ (C) fluxes from the different mangroves (Timonha River, control site; Cocó River, affected by urban wastes; and Jaguaribe River, affected by shrimp farming). For the SCS, CO$_2$ and CH$_4$ fluxes, the averages values followed by different capital letters present significative different values (P < 0.005). For the SCS$_{EQV}$, the averages values followed by different lowercase letters present significative different values (P < 0.005).

(A)

(r = 0.747; P < 0.0001; n = 60)

(B)

(r = 0.781; P < 0.0001; n = 60)
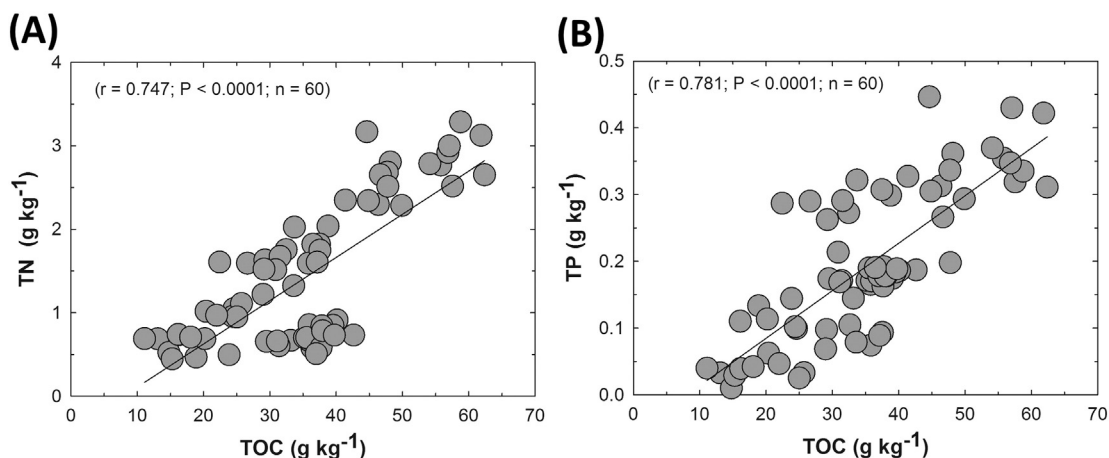
Fig. 6. Correlation between TOC and TN (A); and TOC and TP (B).

2001). These metabolic pathways (Fe^{3+} and SO_4^{2-} reduction) have a lower energetic performance compared to aerobic metabolism, around 14.7 and 13.3%, respectively (Reddy et al., 1986). In fact, the organic C contents obtained for mangrove soils are, on average, up to 4.5 times the TOC values quantified for other semiarid tropical ecosystems soils, such as the *Caatinga* (Sousa et al., 2012), 2.5 times the content of the *Cerrado* soils, the most extensive Brazilian biome (Bayer et al., 2006) or 1.4 times the content of the soils of the Amazon rainforest (Kauffman et al., 1995).

The highest TN and TP contents were found in the mangrove from Jaguaribe River. This mangrove is characterized as an area with an intense anthropogenic impact, especially shrimp farming (Silva and Souza, 2006). This activity is known by its necessity of huge inputs of N and P, but only a small portion (35.5 and 6.1% of the total N and P input, respectively) is retained in shrimp tissues (Páez-Osuna et al., 1997), resulting in high emission factors (1.9 and 0.23 t km^{-2} yr^{-1} of N and P, respectively; Lacerda et al., 2006). Thus, the disposal of wastewater rich in N and P from shrimp farming ponds resulted in an accumulation of these nutrients (Lacerda et al., 2006). The significant correlations between TOC and TN (r = 0.747; P < 0.0001 n = 60; Fig. 6A) and TP (r = 0.781; P < 0.0001, n = 60) indicate that these nutrients are found mainly in organic compounds, emphasizing the importance of studies on C dynamics for understanding the nutrient geochemical processes in the mangroves soils.

The $Fe_{REACTIVE}$ and Fe_{PYRITE} contents showed a negative correlation with the sand content of the samples (Fig. 7). This fact highlights the role of soil texture on the Fe availability for the metabolic process of reducing Fe oxyhydroxides. In mangrove soils, the reduction of Fe oxyhydroxides, followed by sulfate reduction, leads to the formation of iron sulfides, e.g., pyrite (FeS_2), mackinawite (FeS) and greigite (Fe_3S_4) (Nóbrega et al., 2013; Otero et al., 2009). These sulfide species present a significant environmental importance, especially in controlling trace metal bioavailability (Bayen, 2012; Berner, 1970, 1983; Huerta-Diaz and Morse, 1992). Since the soil texture directly influences the availability of $Fe_{REACTIVE}$, an electron acceptor more energetic than SO_4^{2-} and CO_2 (electron acceptor used in the methanogenesis), it can be assumed that in soils with a finer texture the microbial metabolism extends reducing Fe oxyhydroxides and inhibiting the production of CH_4 (Canfield, 1994; Koretsky et al., 2006).

The dissolved organic carbon (DOC) consists of a range of molecules from simple sugars and acids to complex humic substances produced by the decomposition of the litter but also directly secreted as root exudates. Thus, the concentration of DOC depends on factors such as the productivity of vegetation and carbon consumption by microorganisms (Van Den Berg et al., 2012; Weston and Joye, 2005). The DOC is a fraction of the labile organic matter of high importance for the microbial metabolism regulating microbiological metabolic processes. (Weston

and Joye, 2005). The highest DOC values were found in Timonha (mean value: 9.0 ± 0.6 mmol l^{-1}), followed by Jaguaribe (average: 7.9 ± 1.3 mmol l^{-1}) and Cocó Rivers (average: 7.9 ± 0.3 mmol l^{-1}). Similarly, the highest SCS was quantified for the Timonha mangrove (average: 14.4 ± 1.1 kg m^{-2}) followed by Cocó and Jaguaribe (average: 8.3 ± 3.0 and 8.3 ± 1.9 kg m^{-2}, respectively). The greater C bioavailability and, especially, higher concentrations of DOC in Timonha River mangrove would promote greater microbial activity increasing CO_2 flux. The lower DOC concentrations at Cocó and Jaguaribe would limit this metabolic process (Figs. 4D and 5B).

In addition to the higher DOC concentration, the differences found in the DOP values of the three areas point to significant differences in the metabolism of the three areas. Since the Timonha mangrove presented the lowest DOP (mean: 58.1 ± 13.4%), it can be assumed that sulfate reduction occurs less intensively in this environment and that the microbial metabolism occurs by more energetic pathways (Araújo et al., 2012; Nóbrega et al., 2013) resulting in higher CO_2 emissions (Fig. 5B).

Conversely, the higher CO_2 flux from the Timonha did not result in lower SCS or SCS_{EQV}. This fact suggests that, at this site, there is a higher organic matter input from the vegetation, which is better preserved from anthropogenic impacts (Silva and Souza, 2006). On the other hand, it can be assumed that the anthropogenic impacts resulted in the reduction of the organic C input and/or to an intensification of the CO_2 flux during a short period (prior to this study measurements), which would reduce the SCS (and SCS_{EQV}). In fact, anthropogenic impacts (e.g., tree removal) results in quick and significant increase in CO_2 and CH_4 emissions, with a declining trend during the time (Lovelock et al., 2011; Lang'at et al., 2014). As labile organic carbon was consumed during this initial peak of GHG emission, it would be
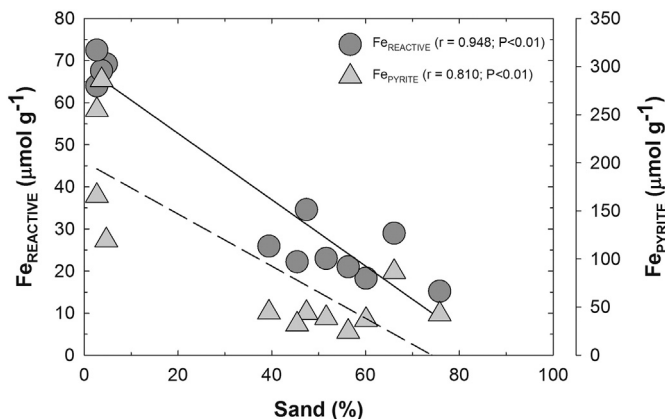
Fig. 7. Correlation between sand content and $Fe_{REACTIVE}$; and between sand and Fe_{PYRITE}.

Table 1
CO_2 and CH_4 emission from mangroves around the world under different climatic conditions.

Location	Climate	Precipitation $(mm\ yr^{-1})$	Average temperature $(°C)$	CO_2 flux $(mg\ m^{-2}\ h^{-1})$	CH_4 flux $(\mu g\ m^{-2}\ h^{-1})$	Reference
Mornington Peninsula, Victoria, Australia	Temperate	719	19	45.6	25.1	Livesley and Andrusiak (2012)
Moreton Bay, Queensland, Austrália	Subtropical	1155	15–24	n.d.	20–350	Kreuzwieser et al. (2003)
Dar es Salaam, Tanzania	Humid tropical	1100	28–31	70–160	7–233	Kristensen et al. (2008b)
Shenzhen, China	Subtropical monsoonal	1927	22	24.6–904.6	190.6–4390.9	Chen et al. (2010)
Chelmer, South East Queensland, Australia	Subtropical	1146	20.4	n.d	3.0–17370.0	Allen et al. (2007)
Hong Kong, China	Subtropical monsoonal	2383	23.1	20.2–74.4	96.5–269.8	Chen et al. (2011)
North Sulawesi, Indonesia	Equatorial	2661	20–28	0–170.7	0–210.24	Chen et al. (2014)
Sawi Bay, Thailand	Tropical monsoonal	908	23.6	30.36–96.8	n.d.	Alongi et al. (2001)

n.d.: not determined.

expected a decline on CO_2 since recalcitrant organic C proportionally accumulates in soil (Lovelock et al., 2011).

Based on the average CO_2 emission of the three areas, it is possible to estimate that mangroves of Ceará emit about 43.9 ± 21.1 Gg $CO_2\ yr^{-1}$, corresponding to a minimum portion of the Brazilian CO_2 emissions (380 Tg CO2; Olivier and Peters, 2010). Although the mangroves are considered marine environments that mostly emit CO_2 to the atmosphere (Allen et al., 2007; Chen et al., 2012), the results obtained in this study (average of three areas equal to 27.1 ± 13.3 mg $CO_2\ m^{-2}\ h^{-1}$ 1) indicates that the mangrove soils emit lower amounts of CO_2 compared to agricultural areas (average 1310 mg $CO_2\ m^{-2}\ h^{-1}$; La Scala et al., 2006).

Regarding the methane emission, the CH_4 fluxes recorded are in accordance with the physicochemical conditions of the studied mangroves. The higher CH_4 flux was recorded for the Jaguaribe River (average: $8.8 \pm 13.8\ \mu g\ m^{-2}\ h^{-1}$), the site with lower Eh, higher DOP and TOC, whereas the other mangroves presented lower CH_4 flux, higher Eh, and a lower DOP. Two reasons may be influencing the low CH_4 flux within these environments. For methanogenesis to occur, the depletion of the more energetic electron acceptors is necessary $(O_2 \rightarrow NO_3^- \rightarrow$ Mn oxyhydroxides $\rightarrow$ Fe oxyhydroxides and SO_4^{2-}), and then, methanogen metabolism uses CO_2 or other methyl compounds (Kristensen et al., 2008a). In mangrove soils, the sulfate is directly supplied via the seawater and, because of its high concentration $(2650\ mg\ l^{-1}$; Driscoll, 1989) it is an almost inexhaustible supply. Furthermore, in semiarid mangrove soils with a lower DOP compared to humid tropical mangroves (Nóbrega et al., 2013), microbial metabolism is maintained at Fe reduction pathways, avoiding the CO_2 consumption for methanogenesis. Moreover, the oxidation of CH_4 by methanotrophic microorganisms in such environments would be able to reduce the possible emission of CH_4 (Kristensen et al., 2008a, 2008b). In fact, the methane emission from our results is considerably lower than those recorded for other tropical humid mangrove soils, as occurred for temperate mangrove, at same vegetation stand (Table 1).

Despite the low emissions of CO_2 and CH_4 derived from studied mangrove soils, anthropogenic and natural changes may alter the ability of these ecosystems to absorb carbon, making them important sources of GHG (Lovelock et al., 2010; Yu et al., 2006). The vegetation removal and drainage of mangrove areas restrict hydromorphism, accelerating the process of oxidation of soil organic matter (Lovelock et al., 2011). Similarly, the fertilization of mangroves by effluents rich in N, e.g., effluent from shrimp farming, can accelerate the decomposition of organic matter reducing the C content and increasing GHG emissions (Chmura, 2011; Nóbrega et al., 2013). On the other hand, the discharge of effluents rich in the labile organic matter can increase microbial metabolism (Purvaja and Ramesh, 2001) or extend waterflooding periods (Marchand et al., 2011), restricting the availability of sulfate as an electron acceptor and resulting in the methanogenesis.

Since the study area is in the Brazilian semi-arid coast, with two well-defined seasons (IPECE, 2010; Sales, 2008; Silva and Souza, 2006), the results obtained in this study, during the rainy season, may present a considerable variation when compared to other studies during the dry season. As mentioned in the literature, seasonal variations lead to substantial changes in the metabolism of the Brazilian semi-arid mangrove soils (for more information, see Nóbrega et al., 2013). Thus, further studies are needed to verify the effect of seasonality on the emission of greenhouse gases during the dry season, since the rainfall distribution along the year may affect the temperature, characteristics, and decomposition rate of the organic matter, and also the O_2 diffusion through the soil, affecting soil biogeochemical processes and microbial metabolic pathways (Kristensen et al. 2008a, 2008b).

5. Conclusions

The CO_2 emissions are highly influenced by soil conditions. The highest CO_2 fluxes were recorded for the undisturbed mangrove, which had a larger amount of dissolved carbon (labile), greater C stock, and lower pyritization degree. Although they are considered marine areas that contribute most to global warming, CO_2 emission rate of mangroves is about 2% of the issue caused by agriculture. The anthropogenic impacts seem to have decreased the organic C input to soils and intensified the CO_2 emission prior to the measurements.

The little methane flux is due to the constant supply of high energy electron acceptors (e.g., iron and sulfate) than CO_2, the substrate used by microorganisms for methanogenesis. However, the predominance of anoxic conditions and a higher degree of pyritization may drive the microbial metabolism to methanogenesis.

Further studies are needed to see how seasonal climate variations work in the emission of CO_2 and CH_4 in semiarid mangroves in Brazil.

Acknowledgments

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