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## Short Communication

# Tidal variability of CO<sub>2</sub> and CH<sub>4</sub> emissions from the water column within a *Rhizophora* mangrove forest (New Caledonia)☆

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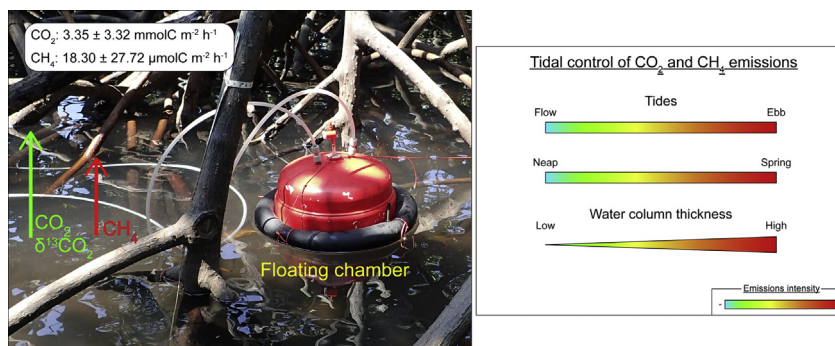
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## HIGHLIGHTS

- CO<sub>2</sub> and CH<sub>4</sub> fluxes from the water column were studied within a mangrove forest.
- Mean emissions were 3.35 mmolC m<sup>-2</sup> h<sup>-1</sup> for CO<sub>2</sub>, and 18.30 μmolC m<sup>-2</sup> h<sup>-1</sup> for CH<sub>4</sub>.
- δ<sup>13</sup>CO<sub>2</sub> ranged from -26.9‰ to -8.6‰, suggesting a mixing between different sources.
- CO<sub>2</sub> and CH<sub>4</sub> emissions were 1.9 and 5.5 times higher during ebb than during flow.
- Spring tides induced higher CO<sub>2</sub> and CH<sub>4</sub> emissions than neap tides.

## GRAPHICAL ABSTRACT



## ABSTRACT

We performed a preliminary study to quantify CO<sub>2</sub> and CH<sub>4</sub> emissions from the water column within a *Rhizophora* spp. mangrove forest. Mean CO<sub>2</sub> and CH<sub>4</sub> emissions during the studied period were 3.35 ± 3.62 mmolC m<sup>-2</sup> h<sup>-1</sup> and 18.30 ± 27.72 μmolC m<sup>-2</sup> h<sup>-1</sup>, respectively. CO<sub>2</sub> and CH<sub>4</sub> emissions were highly variable and mainly driven by tides (flow/ebb, water column thickness, neap/spring). Indeed, an inverse relationship between the magnitude of the emissions and the thickness of the water column above the mangrove soil was observed. δ<sup>13</sup>CO<sub>2</sub> values ranged from -26.88‰ to -8.6‰, suggesting a mixing between CO<sub>2</sub>-enriched pore waters and lagoon incoming waters. In addition, CO<sub>2</sub> and CH<sub>4</sub> emissions were significantly higher during ebb tides, mainly due to the progressive enrichment of the water column by diffusive fluxes as its residence time over the forest floor increased. Eventually, we observed higher CO<sub>2</sub> and CH<sub>4</sub> emissions during spring tides than during neap tides, combined to depleted δ<sup>13</sup>CO<sub>2</sub> values, suggesting a higher contribution of soil-produced gases to the emissions. These higher emissions may result from higher renewable of the electron acceptor and enhanced exchange surface between the soil and the water column. This study shows that CO<sub>2</sub> and CH<sub>4</sub> emissions from the water column were not negligible and must be considered in future carbon budgets in mangroves.

### Keywords:

Water to atmosphere fluxes  
Greenhouse gas  
Blue carbon  
Carbon dioxide isotope  
Semi-arid mangrove forest

## 1. Introduction

Mangroves are considered as major ecosystems in the carbon cycle along tropical and subtropical coastlines, being among the most efficient blue carbon sinks (Kauffman et al., 2011). Due to their high primary productivity, estimated at 218 ± 72 TgC year<sup>-1</sup> (Bouillon et al.,

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2008), and their long-term carbon storage capacities (Donato et al., 2011), mangroves have been recognized as having a key role in climate change mitigation (Howard et al., 2017; Mcleod et al., 2011). However, part of mangroves primary productivity is mineralized in their soils, producing greenhouse gas (GHG) that can be subsequently emitted towards the atmosphere (Chen et al., 2014). Among GHG, methane may be of major concern due to its global warming potential, 34 times higher than CO<sub>2</sub> using a 100 year time frame and climate carbon feedback (Stocker et al., 2013). In anoxic mangrove soils, when electron acceptors such free oxygen, metal oxides, nitrates, and sulfates have been exhausted, methanogenesis can occur. Recently, it was demonstrated that sulfate reducing and methanogens microorganisms can coexist in mangrove soils and it was thus suggested that methane emissions have been underestimated (Chauhan et al., 2015; Lyimo et al., 2009).

In mangrove soils, organic matter (OM) decay processes depend on numerous factors, including waterlogging (Kristensen et al., 2008a). In fact, mangroves are subjected to tidal cycles that influence the redox characteristics of their soils, modifying the rate of GHG production. In addition, tides can also influence GHG emissions towards the atmosphere since gas diffusion differs when the soil is immersed or unsaturated. Recently, many studies focused on CO<sub>2</sub> or CH<sub>4</sub> emissions at the soil-air interface at low tide (Bulmer et al., 2015; Chanda et al., 2013; Chauhan et al., 2015; Chen et al., 2016; Chen et al., 2010; Leopold et al., 2013, 2015; Livesley and Andrusiak, 2012; Wang et al., 2016), or at the water-air interface in adjacent tidal creeks (Borges et al., 2003; Bouillon et al., 2003b; Call et al., 2015; Maher et al., 2015). However, to our knowledge, no study focused on water to atmosphere GHG emissions when the forest is inundated, which may frequently occur, depending on the tidal range and the position of the forest in the intertidal zone.

Stable isotope of carbon ( $\delta^{13}\text{C}$ ) is a widely used tool for studying carbon dynamic in natural environments (Gonneea et al., 2004; Graham et al., 2001; Lu et al., 2016; Yamamuro, 2000), including the partitioning of the different sources (Midwood and Millard, 2011; Millard et al., 2010; Paterson et al., 2009). In mangrove ecosystems, mangrove litter, benthic microalgae, phytoplankton and seagrass detritus are the main OM sources (Kristensen et al., 2008a), and the latter may be distinguishable thanks to their specific  $\delta^{13}\text{C}$  values. Marine OM has typical value of  $\delta^{13}\text{C}$  ranging from  $-30$  to  $-16\%$ , whereas mangroves plants are C3 photosynthetic pathways, and therefore produce OM that have a  $\delta^{13}\text{C}$  value ranging from  $-32$  to  $-21\%$  (Lamb et al., 2006). In addition, due to a low carbon fractionation during respiration processes (Lin and Ehleringer, 1997; Maher et al., 2015), the  $\delta^{13}\text{C}$  of the CO<sub>2</sub> produced is close to the  $\delta^{13}\text{C}$  value of its source. Recent development of advanced technologies such as cavity ring-down spectroscopy (CRDS) allows high resolution in situ measurements of  $\delta^{13}\text{CO}_2$ . Therefore, these new analytical means could help to identify the origins of the CO<sub>2</sub> emitted from mangrove ecosystems.

Within this context, the present study aimed to (i) quantify the CO<sub>2</sub> and CH<sub>4</sub> emissions at the water-air interface within a *Rhizophora* spp. mangrove forest, (ii) evaluate the variability of these emissions along tidal cycles, and (iii) identify the origin of the CO<sub>2</sub> fluxes measured. To reach our goals, we measured CO<sub>2</sub> and CH<sub>4</sub> fluxes, as well as  $\delta^{13}\text{CO}_2$  values, in the field, using a dark floating chamber connected to a cavity ring-down spectrometer analyzer (CRDS), along different tidal cycles from neap to spring tides.

## 2. Material and methods

### 2.1. Study site

The present study was conducted in the mangrove of Ouemo (22°16'50"S, 166°28'16"E), in New Caledonia, a French overseas archipelago located in the South Pacific (21°21'S, 165°27'E). The studied mangrove was dominated by three *Rhizophora* mangrove species: *R. stylosa*, *R. samoensis* and *R. selala*. Climate in the region is semi-arid

and strongly influenced by the inter-tropical convergence zone and by the El Niño Southern Oscillation (ENSO). Average air temperature varied between 20.5 and 26.6 °C, with a mean annual precipitation of 1070 mm (data from [meteofrance.com](http://meteofrance.com)). The tidal regime is semi-diurnal, with a tidal range ranging from 1.10 to 1.70 m.

### 2.2. Gas fluxes measurements

CO<sub>2</sub>,  $\delta^{13}\text{CO}_2$  and CH<sub>4</sub> measurements were performed using a dark custom-built floating chamber (466 cm<sup>2</sup>; 5050 cm<sup>3</sup>) connected to a G2131-*i* CRDS analyzer (Picarro Inc., Santa Clara, CA, USA) that measures gas concentrations at a frequency of 1 Hz. Guaranteed precision of the analyzer are 200 ppb + 0.05% of reading, 50 ppb + 0.05% of reading and 0.1‰, for CO<sub>2</sub> and CH<sub>4</sub>, and  $\delta^{13}\text{CO}_2$ , respectively. Accuracy of the CRDS analyzer was periodically checked using certified N<sub>2</sub> (0 ppm CO<sub>2</sub> and CH<sub>4</sub>), CO<sub>2</sub> (503 ppm) and CH<sub>4</sub> (100 ppm) gas standard samples (Calgaz, Air Liquide, USA).

We are aware that floating chambers may induce a bias in flux measurements during windy conditions or with high current velocity that induce artificial turbulences and, as a result, increase fluxes (Kremer et al., 2003; Yang et al., 2014). However, in low turbulence environment, like inside the mangrove forest where the wind is almost null, and the water flow is slow, the floating chamber technique can be a powerful method (Lorke et al., 2015; Vachon et al., 2010). Thus, we feel confident about the validity of our measurements. In addition, floating chambers have the capability to capture ebullition events that may account for a large proportion of the gas transferred to the atmosphere, particularly CH<sub>4</sub> (Chuang et al., 2017).

Measurements were performed every three weeks, from December 2016 to September 2017, at a single sampling station. Measurements were done during sunny days, with the slack high tide around noon, and included different tidal regimes. During neap tides, the tidal range varied from 1.10 to 1.25 m, which corresponded to a water column thickness above the mangrove sediment of 15 to 30 cm at the maximum of the high tide. During spring tides, the tidal range varied from 1.25 to 1.55 m, and, therefore, the water column thickness at the maximum of the high tide ranged from 30 cm to 60 cm. Measurements were performed all along the high tide, from the beginning of the flow to the end of the ebb. For each incubation, an integrating period of 3 to 6 min was chosen, depending on the linearity of the signal. Therefore, 19 to 40 measurements were performed during each campaign, resulting in a total of 284 flux measurements.

In addition, before each incubation, water level was measured thanks to a water gauge, and air temperature was recorded thanks to a handheld Skymate SM-19 thermometer.

### 2.3. Flux calculation

Water to atmosphere fluxes of CO<sub>2</sub> and CH<sub>4</sub> were integrated as a function of time, and calculated using the following formula:

$$F_{(\text{CO}_2, \text{CH}_4)} = (d(\text{CO}_2, \text{CH}_4)/dt) * V / (R * S * T) * 3.6$$

where F is the water to atmosphere fluxes of CO<sub>2</sub> or CH<sub>4</sub> (mmolC m<sup>-2</sup> h<sup>-1</sup>); d(CO<sub>2</sub>, CH<sub>4</sub>) / dt is the variation in CO<sub>2</sub> or CH<sub>4</sub> as a function of time (ppm s<sup>-1</sup>); V is the total volume of the system (m<sup>3</sup>); R is the ideal gas constant of 8.205746 10<sup>-5</sup> (atm m<sup>3</sup> K<sup>-1</sup> mol<sup>-1</sup>); T is the absolute air temperature (K); and S is the area of the bottom of the incubation chamber (m<sup>2</sup>).

### 2.4. $\delta^{13}\text{CO}_2$

To measure the isotopic value of the CO<sub>2</sub> ( $\delta^{13}\text{CO}_2$ ) released from the water column, we used a Keeling plot approach (Keeling, 1958, 1961; Pataki et al., 2003). By plotting the  $\delta^{13}\text{CO}_2$  value CO<sub>2</sub> as a function of the inverse of the CO<sub>2</sub> concentration ( $\delta^{13}\text{CO}_2 = f(1/\text{CO}_2)$ ) during each incubation, the intercept of a linear regression with the y-axis is equivalent to the  $\delta^{13}\text{CO}_2$  value of the flux.

In addition, three supplementary incubations were realized at high tide outside the mangrove forest to evaluate the  $\delta^{13}\text{CO}_2$  value of the  $\text{CO}_2$  produced within the water column in the lagoon.

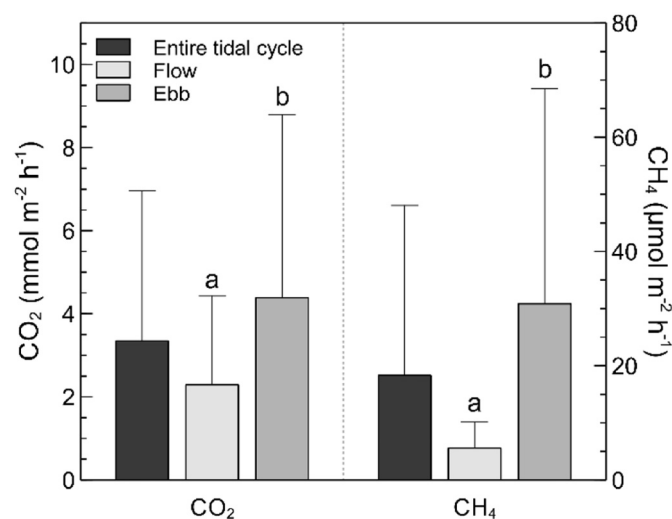
## 2.5. Statistical analyses

Student's *t*-tests were used to test the significant differences ( $p < 0.05$ ) in the emissions between flow and ebb tides as well as between spring and neap tides. All statistical analyses were performed under R software version 3.3.1 (R Development Core Team, 2008).

## 3. Results and discussion

$\text{CO}_2$  and  $\text{CH}_4$  emissions from the water column to the atmosphere varied from 0.13 to 18.41  $\text{mmolC m}^{-2} \text{h}^{-1}$  and from 0.18 to 172.07  $\mu\text{molC m}^{-2} \text{h}^{-1}$ , respectively (Fig. 1). Thus, when converted into  $\text{CO}_2$ -equivalent and considering its 100-year global warming potential (Stocker et al., 2013), methane represented 18% of the total emissions measured ( $\text{CO}_2 + \text{CH}_4$ ). Gas transfer to the atmosphere may occur by upward molecular diffusion (Kristensen et al., 2008b) but also through gas bubble ebullition, mainly for methane due to its lower solubility (Barnes et al., 2006; Komiya et al., 2015; Stamp et al., 2013). However, in the present study, considering the linear evolution of  $\text{CO}_2$  and  $\text{CH}_4$  concentrations with time during each flux measurement, we suggest that only the diffusive fluxes were measured. As a consequence, the emissions reported herein may have been under-estimated, particularly methane.

To our knowledge, this study was the first one interested in measuring GHG emissions at the water-air interface within a mangrove forest. Therefore, we decided to compare our results with fluxes from other interfaces (*i.e.* from mangrove soils and creek waters to the atmosphere).  $\text{CO}_2$  emissions were in the same order of magnitude and even higher than from mangrove soils at low tide or from mangrove tidal creeks (Table 1). It was demonstrated that soil surface biofilm may limit GHG emissions from mangrove soils, notably by acting as a physical barrier but also by using the  $\text{CO}_2$  for primary production through photosynthesis (Bulmer et al., 2015; Leopold et al., 2015; Leopold et al., 2013). As a result, some authors reported negative fluxes at the soil surface (*e.g.* Chen et al., 2014; Leopold et al., 2015), which was never the case from the water column in the studied *Rhizophora* forest. Closed canopy and elevated water turbidity probably limited the development of



**Fig. 1.** Mean  $\text{CO}_2$  ( $\text{mmolC m}^{-2} \text{h}^{-1}$ ) and  $\text{CH}_4$  ( $\mu\text{molC m}^{-2} \text{h}^{-1}$ ) (+SD) emissions during the complete tidal cycles ( $n = 284$ ), the flow tides ( $n = 141$ ) and the ebb tides ( $n = 143$ ) in the mangrove of Ouemo for the period December 2016 to September 2017. Different letters indicate significant differences (two-samples *t*-test,  $\text{CO}_2$ :  $t_{(205.66)} = 5.11$ ,  $p < 0.001$ ,  $\text{CH}_4$ :  $t_{(146.3)} = 7.96$ ,  $p < 0.001$ ).

microalgae that might have used the  $\text{CO}_2$  produced in the soil. In addition, low tide fluxes measurements are strictly representative of the surface that is covered by the incubation chamber, and, usually, roots and crab burrows are excluded to avoid overestimations of the fluxes. At the opposite, water-air fluxes integrate the entire soil surface that is flooded by the water, and, therefore, roots and burrows are an important factor to take into account as they represent preferential diffusion pathways for the gases to escape from the sediment. The density of *Rhizophora* roots and crab burrows could not be measured in our study site, however, the density of crab burrows was reported for other mangrove in New Caledonia and was evaluated to 83 burrows  $\text{m}^{-2}$  for the fiddler crab *Uca* spp. (Nielsen et al., 2003), and from 8.9 to 29.1 crabs  $\text{ha}^{-1}$  for the mud crab *Scylla serrata* (Dumas et al., 2012).

However, regarding  $\text{CH}_4$ , some studies reported much higher values from mangrove soils but lower from tidal creeks (Table 1). When  $\text{CH}_4$  diffuses from anoxic mangrove soils into oxic lagoon water, it may be subject to aerobic oxidation by methane-oxidizing bacteria or to photo-oxidation (Morana et al., 2015; Smith et al., 2003), therefore limiting emissions at the water-air interface both in mangrove forests and in tidal creeks. We thus suggest that further measurements of GHG emissions must be performed in mangroves at high tide with different physiographic conditions. We also suggest including these results in future mangrove carbon budgets to make them more accurate, this ecosystem being flooded part of the time.

Our results demonstrate that  $\text{CO}_2$  and  $\text{CH}_4$  fluxes were highly variable with tides. As the thickness of the water column above the mangrove soil increased,  $\text{CO}_2$  and  $\text{CH}_4$  emissions decreased (Fig. 2a, b, c and d). The  $\delta^{13}\text{CO}_2$  value of the  $\text{CO}_2$  fluxes measured at the lowest tidal level was  $-26.88\%$  (Fig. 2e), which was close to the  $\delta^{13}\text{C}$  values of *Rhizophora* roots, ranging from  $-32$  to  $-25\%$  (Weiss et al., 2016), and organic matter, ranging from  $-30$  to  $-20\%$  (Bouillon et al., 2003a; Saintilan et al., 2013; Weiss et al., 2016). Oppositely, the  $\delta^{13}\text{CO}_2$  value measured at the highest tidal level that was  $-8.6\%$  (Fig. 2e and f), which was similar to the values of  $\delta^{13}\text{CO}_2$  measured in the lagoon outside the mangrove. Consequently, we suggest that (i) the variability of the  $\text{CO}_2$  fluxes measured resulted from a mixing between these two sources, *i.e.* the  $\text{CO}_2$  produced within the soil and the one produced within the water column, and that (ii) emissions decreases with the increasing water column thickness resulted from the dilution of pore waters, enriched in  $\text{CO}_2$ , by lagoon waters. We also suggest that few biogeochemical processes affected  $\text{CO}_2$  dynamic within the water column due to (i) its low thickness that implied a low residence time of the gas, and (ii) limited photosynthetic processes resulting from dense canopy and water turbidity, as explained earlier. Regarding  $\text{CH}_4$ , water mixing and aerobic oxidation, within the water column, as it was observed in other studies (Abril et al., 2007; Bouillon et al., 2007; Dutta and Mukhopadhyay, 2016) may partly explain the results obtained. However, measurements of both  $\delta^{13}\text{CH}_4$  and dissolved oxygen are needed to comfort these hypotheses.

In addition, significant higher emissions were measured during the ebb than during the flow (two-samples *t*-test,  $\text{CO}_2$ :  $t_{(205.66)} = 5.11$ ,  $p < 0.001$ ,  $\text{CH}_4$ :  $t_{(146.3)} = 7.96$ ,  $p < 0.001$ ), but also during spring tides than during neap tides ( $\text{CO}_2$ ,  $t_{(180.56)} = -4.60$ ,  $p < 0.001$ , and  $\text{CH}_4$ ,  $t_{(134.1)} = -5.32$ ,  $p < 0.001$ ) (Fig. 2a, b, c and d). We suggest that these differences may result from a combination of different factors including: residence times of the water in the soil, volume of lagoon water entering the mangrove, area of submerged mangrove, and electron acceptor renewal.

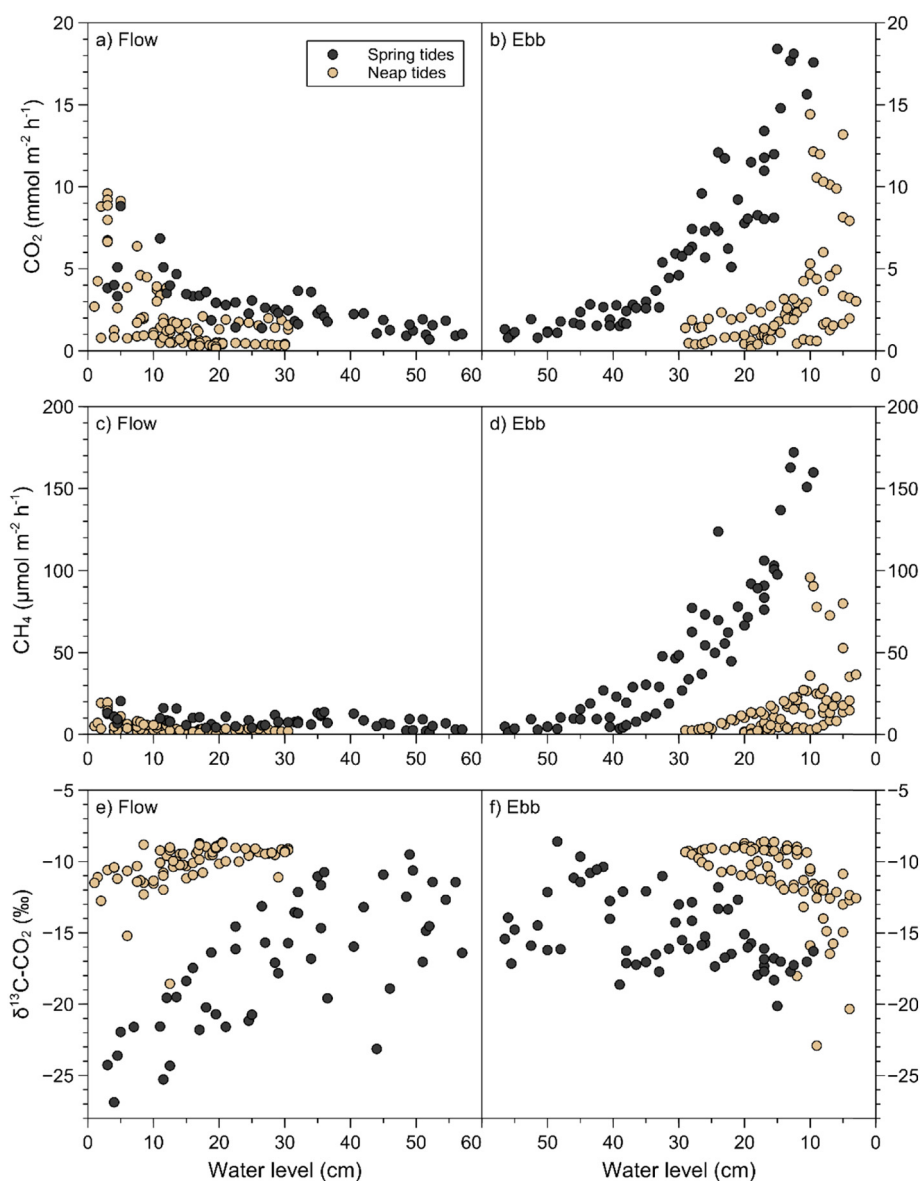
During neap tides,  $\text{CO}_2$  emissions reached up to 9.59  $\text{mmolC m}^{-2} \text{h}^{-1}$  at the beginning of the rising tide, and up to 14.42  $\text{mmolC m}^{-2} \text{h}^{-1}$  at the end of the ebb tide (Fig. 2a and b). Meanwhile, as water thickness decreased during ebb, the  $\delta^{13}\text{CO}_2$  values showed clearly an increased contribution of the  $\text{CO}_2$  originated from mangrove soils, with more depleted values at the end of the ebb tides (Fig. 2e and f). Several forcing factors may enhance the exchanges of gaseous compounds between the soil and the overlying water, including: (i) flushing of the upper centimeters



**Table 1**

Various dark CO<sub>2</sub> (mmolC m<sup>-2</sup> h<sup>-1</sup>) and CH<sub>4</sub> (μmolC m<sup>-2</sup> h<sup>-1</sup>) emissions from mangrove forests during emersion periods, and from mangrove creeks and estuaries.

Location	Climate	CO <sub>2</sub> (mmolC m <sup>-2</sup> h <sup>-1</sup> )	CH <sub>4</sub> (μmolC m <sup>-2</sup> h <sup>-1</sup> )	Reference
Mangrove waters New Caledonia	Semi-arid	0.13 to 18.41	0.18 to 172.07	This study
Mangrove soils New Zealand	Temperate	7.02 ± 1.91	–	Bulmer et al. (2015)
New Caledonia	Semi-arid	–0.71 to 2.41	–	Leopold et al. (2015)
China	Subtropical	6.92 to 20.56	34.24 to 5168.60	Chen et al. (2010)
China	Subtropical	–0.19 to 4.62	21.56 to 1919.68	Wang et al. (2016)
Indonesia	Tropical	–1.34 to 3.88	–6.05 to 13.14	Chen et al. (2014)
Tanzania	Tropical	1.50 to 3.67	0 to 3.65	Kristensen et al. (2008b)
Mangrove creeks and estuaries Brazil	Semi-arid	0.62 ± 0.30	0.0000093	Nóbrega et al. (2016)
Australia	Subtropical	0.38 to 26.21	0.54 to 26.38	Call et al. (2015)
Florida	Subtropical	–	–2.60 to 9.61	Cabezas et al. (2017)
Australia	Subtropical	0.79 to 2.92	0.29 to 2.13	Maher et al. (2015)
India	Tropical	–	0.08 to 5.61	Biswas et al. (2007)
India	Tropical	–	0.37	Dutta et al. (2015)



**Fig. 2.** Emissions of CO<sub>2</sub> and CH<sub>4</sub> fluxes, and δ<sup>13</sup>C-CO<sub>2</sub> values (‰) as a function of the water level above the sediment: (a, c and e) during flow tides, and (e, d and f) during the ebb tides.

of soil driven by bottom currents inducing pressure gradients at the soil surface, concept of “skin circulation” introduced by Billerbeck et al. (2006); (ii) macrofaunal burrowing activities during inundation, causing an increase in soil permeability (Santos et al., 2012); (iii) flushing of crab burrows, the later significantly enhancing the effective surface area of mangrove soils (up to 7-fold), therefore increasing the diffusive fluxes towards the water column (Stieglitz et al., 2000, 2013; Heron and Ridd, 2008). We suggest that the increased residence time of the water during inundation resulted in enhanced exchanges across the soil-water interface due to the different processes listed above, inducing its enrichment in gaseous compounds, and explaining thus the higher emissions measured during the ebb than during the flow. Additional processes may be involved for CH<sub>4</sub> since the difference between the beginning of the flow and the end of the ebb was much higher than for CO<sub>2</sub> (Fig. 2); CH<sub>4</sub> concentrations was <21 μmolC m<sup>-2</sup> h<sup>-1</sup> during the flow and reached >170 μmolC m<sup>-2</sup> h<sup>-1</sup> during the ebb when the water levels were minimum (Fig. 2c and d). During low tide, atmospheric air can penetrate deeper in the soil, limiting its anoxic character and thus CH<sub>4</sub> production (Kristensen et al., 2008a). However, although its production can occur deeper in the soil, CH<sub>4</sub> may be oxidized during its transit to the atmosphere within the soil, resulting in the low emissions measured at the beginning of the flow. Conversely, at the end of the ebb, most of electron acceptors may have been exhausted due to the installation of an anoxic environment during the high tide, and thus, methanogenesis may occur, resulting in higher CH<sub>4</sub> emissions.

During spring tides, emissions intensity differed from neap tides. If fluxes were not significantly higher during the flow, they were during the ebb, with CO<sub>2</sub> and CH<sub>4</sub> emissions reaching up to 18.41 mmolC m<sup>-2</sup> h<sup>-1</sup> and 172.07 μmolC m<sup>-2</sup> h<sup>-1</sup>, respectively (Fig. 1 and Fig. 2a, b, c and d). One possible explanation is a higher renewable of the electron acceptors pool within the soil during spring tide, which enhanced the microbial activity and consequently greenhouse gas production. Then, at low tide, the water level within the soil may be lower during spring tide, resulting in higher contribution of the soil deep layers to CH<sub>4</sub> emissions, as gas diffusion is higher in air than in water. Additionally, higher water level during spring tides may have flooded the upper intertidal zones within the mangrove forest, increasing therefore the exchanges between the surface pore waters and the overlying water column. The flushing of surface pore waters and burrows of this upper intertidal zone, due to changes in hydrostatic pressure along the topographic gradient during ebb, may be involved in the enhancement of the emissions, analogically to the concept of “mangrove tidal pumping”, which has been described to significantly enrich tidal creeks in nutrients, gaseous and dissolved compounds (Call et al., 2015; Dittmar and Lara, 2001; Maher et al., 2013, 2015). In addition, the more depleted δ<sup>13</sup>CO<sub>2</sub> values during ebb of spring tides, in comparison to ebb of neap tides (Fig. 2f), and except at the lowest water column thickness, support the hypothesis of a higher contribution of CO<sub>2</sub> produced within mangrove soils to the water column. Surprisingly, the lowest δ<sup>13</sup>CO<sub>2</sub> values were measured at the beginning of the flow (Fig. 2e), which were close to the δ<sup>13</sup>C values of mangrove soil organic matter or mangrove roots as explain earlier in this study, suggesting than mangrove pore waters strongly dominated the water column composition at this period of the tide, which is clearly different from neap tides (Fig. 2e). This result may be related to the tidal wave spread when entering the mangrove, inducing higher pore water advection during the spring tides notably through crab burrows. However, although higher mean CO<sub>2</sub> and CH<sub>4</sub> emissions were observed for the flow during spring tides, the maximal value reached by the emissions was not higher than during neap tides (Fig. 2a). One possible explanation is that CO<sub>2</sub> and CH<sub>4</sub> did not accumulate within the soil at low tide due to the more efficient diffusion of GHG in air than in water, and thus were rapidly emitted to the atmosphere. When the tide increased, the deep soil pore waters, depleted in δ<sup>13</sup>CO<sub>2</sub>, were transported to the surface, resulting in low δ<sup>13</sup>CO<sub>2</sub>

values emitted at the water surface. This study thus highlighted that tides (flow/ebb, water column thickness, neap/spring) is a key factor controlling CO<sub>2</sub> and CH<sub>4</sub> emissions from the water column during mangrove forests immersion periods. In a future research effort, the influence of other environmental parameters such as seasonal temperature variations should be studied. Although the sampling period in this study encompassed the two main seasons in New Caledonia, they were not entirely covered, and considering the high tidal variability, our data set did not allow us to conclude on a possible seasonal effect.

#### 4. Conclusion

This preliminary study demonstrates that tide characteristics (flow/ebb, water column thickness, neap/spring) drove CO<sub>2</sub> and CH<sub>4</sub> emissions at the water-air interface within the studied *Rhizophora* spp. mangrove forest. Simultaneous measurements of CO<sub>2</sub>, CH<sub>4</sub> and δ<sup>13</sup>CO<sub>2</sub> values highlighted that:

- the water column above the forest floor was a mix between soil pore waters, enriched in gaseous compounds originated from OM decomposition and root respiration, and incoming lagoon water, poor in CO<sub>2</sub> and CH<sub>4</sub> and characterized by enriched δ<sup>13</sup>C values, resulting in lower fluxes when the water column thickness increased,
- the progressive enrichment of the water column in CO<sub>2</sub> and CH<sub>4</sub> by diffusive fluxes, as its residence time over the forest floor increased, induced higher fluxes during the ebb tide than during the flow,
- CO<sub>2</sub> and CH<sub>4</sub> emissions were higher during spring tides than during neap tides possibly due to (i) higher renewable of the electron acceptor pool within the soil that enhanced microorganism's activity, and (ii) flooding of the upper intertidal zones that induced a higher exchange surface between the soil and the water column.

These results also showed that CO<sub>2</sub> and CH<sub>4</sub> emissions were not negligible and therefore, we suggest that these fluxes should be integrated in future carbon budget to make them more accurate. Further studies should now examine the variability of these emissions across mangroves that differ by their physiographic conditions to assess their spatial variability.

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#### Declaration of interest

Authors have no conflict of interest to declare.

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