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Short Communication

Tidal variability of CO_2 and CH_4 emissions from the water column within a *Rhizophora* mangrove forest (New Caledonia)☆

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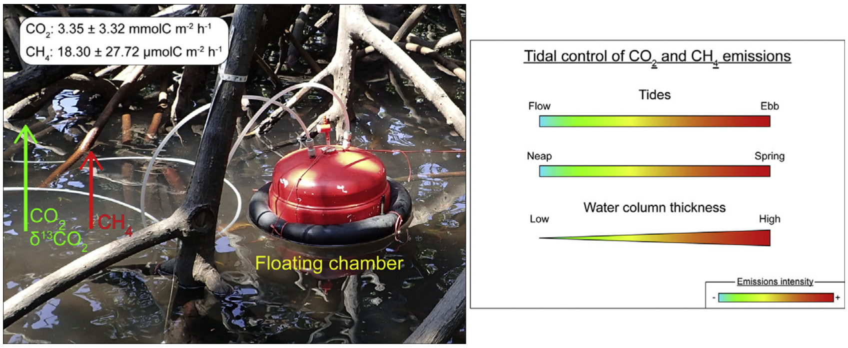
HIGHLIGHTS

- CO_2 and CH_4 fluxes from the water column were studied within a mangrove forest.
- Mean emissions were 3.35 mmolC m^{-2} h^{-1} for CO_2, and 18.30 μmolC m^{-2} h^{-1} for CH_4.
- $\delta^{13}CO_2$ ranged from −26.9‰ to −8.6‰, suggesting a mixing between different sources.
- CO_2 and CH_4 emissions were 1.9 and 5.5 times higher during ebb than during flow.
- Spring tides induced higher CO_2 and CH_4 emissions than neap tides.

GRAPHICAL ABSTRACT



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ABSTRACT

We performed a preliminary study to quantify CO_2 and CH_4 emissions from the water column within a *Rhizophora* spp. mangrove forest. Mean CO_2 and CH_4 emissions during the studied period were 3.35 ± 3.62 mmolC m^{-2} h^{-1} and 18.30 ± 27.72 μmolC m^{-2} h^{-1}, respectively. CO_2 and CH_4 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. $\delta^{13}CO_2$ values ranged from −26.88‰ to −8.6‰, suggesting a mixing between CO_2-enriched pore waters and lagoon incoming waters. In addition, CO_2 and CH_4 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_2 and CH_4 emissions during spring tides than during neap tides, combined to depleted $\delta^{13}CO_2$ 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_2 and CH_4 emissions from the water column were not negligible and must be considered in future carbon budgets in mangroves.

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 $year^{-1}$ (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_2 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 immerged or unsaturated. Recently, many studies focused on CO_2 or CH_4 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 ($\delta^{13}C$) 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 $\delta^{13}C$ values. Marine OM has typical value of $\delta^{13}C$ ranging from −30 to −16‰, whereas mangroves plants are C3 photosynthetic pathways, and therefore produce OM that have a $\delta^{13}C$ 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 $\delta^{13}C$ of the CO_2 produced is close to the $\delta^{13}C$ value of its source. Recent development of advanced technologies such as cavity ring-down spectroscopy (CRDS) allows high resolution in situ measurements of $\delta^{13}CO_2$. Therefore, these new analytical means could help to identify the origins of the CO_2 emitted from mangrove ecosystems.

Within this context, the present study aimed to (i) quantify the CO_2 and CH_4 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_2 fluxes measured. To reach our goals, we measured CO_2 and CH_4 fluxes, as well as $\delta^{13}CO_2$ 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). The tidal regime is semi-diurnal, with a tidal range ranging from 1.10 to 1.70 m.

2.2. Gas fluxes measurements

CO_2, $\delta^{13}CO_2$ and CH_4 measurements were performed using a dark custom-built floating chamber (466 cm^2; 5050 cm^3) 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_2 and CH_4, and $\delta^{13}CO_2$, respectively. Accuracy of the CRDS analyzer was periodically checked using certified N_2 (0 ppm CO_2 and CH_4), CO_2 (503 ppm) and CH_4 (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_4 (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_2 and CH_4 were integrated as a function of time, and calculated using the following formula:

$F_{(CO2,CH4)} = (d(CO_2,CH_4)/dt) * V/(R * S * T) * 3.6$ where F is the water to atmosphere fluxes of CO_2 or CH_4 (mmolC m^{-2} h^{-1}); d(CO_2, CH_4) / dt is the variation in CO_2 or CH_4 as a function of time (ppm s^{-1}); V is the total volume of the system (m^3); R is the ideal gas constant of 8.205746 10^{-5} (atm m^3 K^{-1} mol^{-1}); T is the absolute air temperature (K); and S is the area of the bottom of the incubation chamber (m^2).

2.4. $\delta^{13}CO_2$

To measure the isotopic value of the CO_2 ($\delta^{13}CO_2$) released from the water column, we used a Keeling plot approach (Keeling, 1958, 1961; Pataki et al., 2003). By plotting the $\delta^{13}CO_2$ value CO_2 as a function of the inverse of the CO_2 concentration ($\delta^{13}CO_2 = f(1/CO_2)$) during each incubation, the intercept of a linear regression with the y-axis is equivalent to the $\delta^{13}CO_2$ value of the flux.