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Abstract

Mangrove forests are potentially large biogenic sources of atmospheric hydrogen sulphide (H_2S), featuring among the carbon-richest ecosystems in the world associated with strong soil anoxia and large quantities of sulphates brought by tides. H_2S is highly toxic and acts as a precursor for atmospheric sulphur compounds and sulphate aerosols, which contribute to acid deposition and have implications for global climate change. Therefore, understanding H_2S emissions in mangroves holds great importance. Yet, its range of emissions remains uncertain. In this exploratory study, soil H_2S concentrations were measured during tide stall at both high and low tide in a semi-arid mangrove, which has never been done before. Then, potential H_2S fluxes to the atmosphere were estimated at low tide. Soil concentrations were greater at high tide than low tide, probably due to larger soil anoxia (average of -377 vs -179 mV), with average values of 1.40 ± 0.55 and

0.73 ± 0.32 mmol L^{-1}, respectively. Temperature was a key factor controlling soil concentrations, with higher values in the warm season than in the cold season. Average H_2S emissions ranged from 5.81 ± 2.58 to 28.74 ± 6.98 µg S m^{-2} h^{-1} with a mean value of 14.90 ± 7.90 µg S m^{-2} h^{-1}. This study contributes to reducing the uncertainty in the variation range of H_2S fluxes from mangroves, which may be significant for the global sulphur cycle.

1. Introduction

Mangrove forests are ecosystems composed of C3 halophytic trees growing on the land-sea intertidal continuum on most (sub)tropical coasts of the world. Mangrove forests are renowned for their long-term carbon (C) sequestration potential, which has earned them a place on the "Blue Carbon" ecosystems list (Donato *et al.*, 2011). Their large C sequestration capacity stems from both i) large primary productivity of the trees and ii) oxygen-limited decomposition of soil organic matter (SOM) due to the almost permanently waterlogged conditions, in turn controlled by the local tidal regime. Aerobic oxidation of SOM, the energetically prevailing thermodynamic process, is mostly restricted to the topmost few centimetres of the soil and to micro-aerobic zones of the rhizosphere due to crab burrows and oxygen transfers from the atmosphere down to the soil (Kristensen *et al.*, 2017). Dissimilatory sulphate reduction (DSR), a strictly anaerobic process, is the second dominant SOM decomposition pathway in mangrove soils, accounting for up to 50% of total C mineralization (Kristensen *et al.*, 2008). Hydrogen sulphide (H_2S), produced by DSR (Barton *et al.*, 2014), is the main biogenic sulphur gas emitted from mangroves, contributing up to 70% of total S emissions (Ganguly *et al.*, 2018). H_2S is best known for its strong rotten egg odour and its high toxicity for animal and plant life (Barton *et al.*, 2014), but is also a precursor of atmospheric sulphur dioxide (SO_2), sulphuric acid (H_2SO_4) and sulphate (SO_4) aerosols, which contribute to acid deposition. Additionally, sulphate aerosols impact global climate change, with a potential cooling effect of 0.75 W m^{-2} (Ganguly *et al.*, 2018). According to Watts (2000), H_2S emissions from natural sources are larger than anthropogenic

emissions (4.42 vs 3.30 Tg yr^{-1}). However, the contribution of coastal wetlands remains very uncertain, in particular that of mangrove forests due to a great scarcity of measurement data.

2. Material and methods

In this context, the objectives of this work were to measure soil H_2S concentrations and to estimate potential emissions to the atmosphere from a *Rhizophora* spp. mangrove forest in New Caledonia (Southern hemisphere; 22°16'49.3"S, 166°28'15.3"E). This mangrove ecosystem experiences a semi-diurnal tidal regime (range of 1.10 to 1.70 m), and a tropical wet and dry climate classified as category Aw according to the Köppen-Geiger classification. The region has two distinct seasons: a wet and warm season spanning from November to April, and a dry and cold one from May to October.

To measure porewater H_2S concentrations in the soil, core samples were collected once per month between January and August 2017, during low and high tide. Triplicate porewater samples were extracted from six depths (-0.05 to -0.55 m with a 0.10 m interval) using Rhizon micro-samplers and transferred to gas-sealed vials with a nitrogen headspace (1:1 volume). Each vial was then shaken to achieve gas equilibrium between the dissolved sulfides in the porewater and the gas phase. Subsequently, a subsample of the vial headspace was taken for further analysis. Lastly, a supplementary gas sample was collected 5 cm above the soil during low tide to measure atmospheric H_2S concentration. H_2S concentrations were analysed using gas chromatography equipped with a pulsed flame photometric detector (PFPD, OI Analytical) for H_2S detection (Shimadzu, GC-17A, Japan) and a GS-GasPro capillary column (30 m x 0.32 mm, Agilent Technologies, USA). Analytical conditions were set as follows: injector, oven, and detector temperatures were fixed at 200, 65 and 250 °C, respectively. Injection volume was 1 ml with a 1:20 split. Retention time for H_2S was ~3.6 min. The peak areas were integrated and reported to a 7-points calibration curve created with pure nitrogen as zero and from dilutions of a 25 ppm H_2S gas standard. The conversion

from partial pressure of H_2S in the headspace (ppm) to concentration in the water samples (mmol L^{-1}) were done following Bastviken *et al.* (2004), using Henry's law and a Henry's law constant of 0.1 M atm^{-1} (Sander, 1999).

In addition, an extra core was collected during six campaigns (January to June 2017) to measure redox potential, soil water content, pH, soil density, salinity and soil organic carbon content, both during low and high tide (Jacotot *et al.*, 2004).

H_2S fluxes to the atmosphere were estimated for low-tide periods, when the soil is exposed to the atmosphere, using a soil-atmosphere gradient method (SAGM). The SAGM is based on Fick's first law that relates the gas concentration gradient between two depths with the gas diffusion coefficient in the soil (Ds). The entire calculation procedure and the equations used are detailed in Supplementary Material. The use of SAGM is constrained by the determination of a proper value of the tortuosity factor (ε) that influences Ds. This determination can be done *in-situ* using gas tracers, but also estimated using empirical models. Herein, five values of ε were first determined with empirical models, all based on soil porosity and water content (Step 1 in Supplementary Material). To determine the optimal ε value, we used a dataset from Jacotot *et al.* (2019) consisting of soil CH_4 concentrations, and surface to atmosphere CH_4 fluxes measured using incubation chambers. These measurements were obtained at the same site and on the same date as the H_2S concentrations presented in this study. For detailed information regarding the measurement methodologies employed, please refer to Jacotot *et al.* (2019). Subsequently, the SAGM was applied to calculate five sets of CH_4 fluxes to the atmosphere using the five potentials values of ε (Step 1). To assess the differences between the SAGM-derived CH_4 fluxes and the ones obtained from static chambers, the Normalized Root Mean Square Error (NRMSE) was calculated (Step 2 in Supplementary Material). Finally, the ε value that yielded the lowest NRMSE was selected for the subsequent calculation of H_2S fluxes by SAGM using measurements taken 0.05 m below and 0.05 m above the soil surface.

3. Results and discussion

Our results demonstrated that soil H_2S concentrations varied over an order of magnitude and were driven by both tidal regime and seasonal temperature oscillations (Table 1 and Fig. 1A). Larger concentrations were observed at high tide (1.40 ± 0.55 mmol L^{-1}, 0.34-2.40 mmol L^{-1}) than at low tide (0.73 ± 0.32 mmol L^{-1}, 0.16-1.44 mmol L^{-1}). A possible hypothesis to explain the difference in concentrations between high and low tides is that during high tide, the waters from the lagoon circulating in the soil's interstitial pores may facilitate the renewal of electron acceptors by introducing sulphates. This, along with the strong anoxia of the sediment (redox values between -250 and -400 mV; Fig. 2A in Supplementary Material), could potentially support a high rate of DSR and accumulation of H_2S. However, measurements of sulphate concentrations are necessary to support or reject this hypothesis. Conversely, at low tide the absence of a water column above the soil and a lower soil water content (Fig. 2E in Supplementary Material) allow i) emission of the H_2S produced during high tide at the surface, and ii) oxygen diffusion within the soil, thus favouring aerobic SOM decomposition and H_2S oxidation. In addition, whatever the tidal regime, seasonal differences in soil H_2S concentrations were evidenced, with larger values during the warm season (Fig. 1A). While many factors can influence gas production, considering that all measurements were done during tide stall and that no significant variations in the physical and chemical drivers were observed between the warm and cool seasons except of temperature changes (see in Jacotot *et al.,* 2019), we suggest that H_2S soil concentrations were mainly driven by the seasonal temperature variability. Indeed, the temperature sensitivity of SOM decomposition is a phenomenon widely described in the literatures (*e.g.* Conant *et al.*, 2011; Davidson and Janssens, 2006). Eventually, no clear vertical stratification of H_2S concentrations was observed, at either high or low tide, suggesting a relative homogeneity of the physical and chemical properties of the soil column that drive gas production and oxidation; which is supported by the low variability in depth of the physico-chemical parameters measured (Fig. 2 in Supplementary Material). Lastly, the concentrations measured in our study are comparable to those measured in the mangroves of Belize by Lee *et al.* (2008). However,

these authors observed a large increase in H_2S concentrations below 15 cm depth, which was not the case in our study. This difference may be attributed to the relative homogeneity of the soil column, as discussed above.

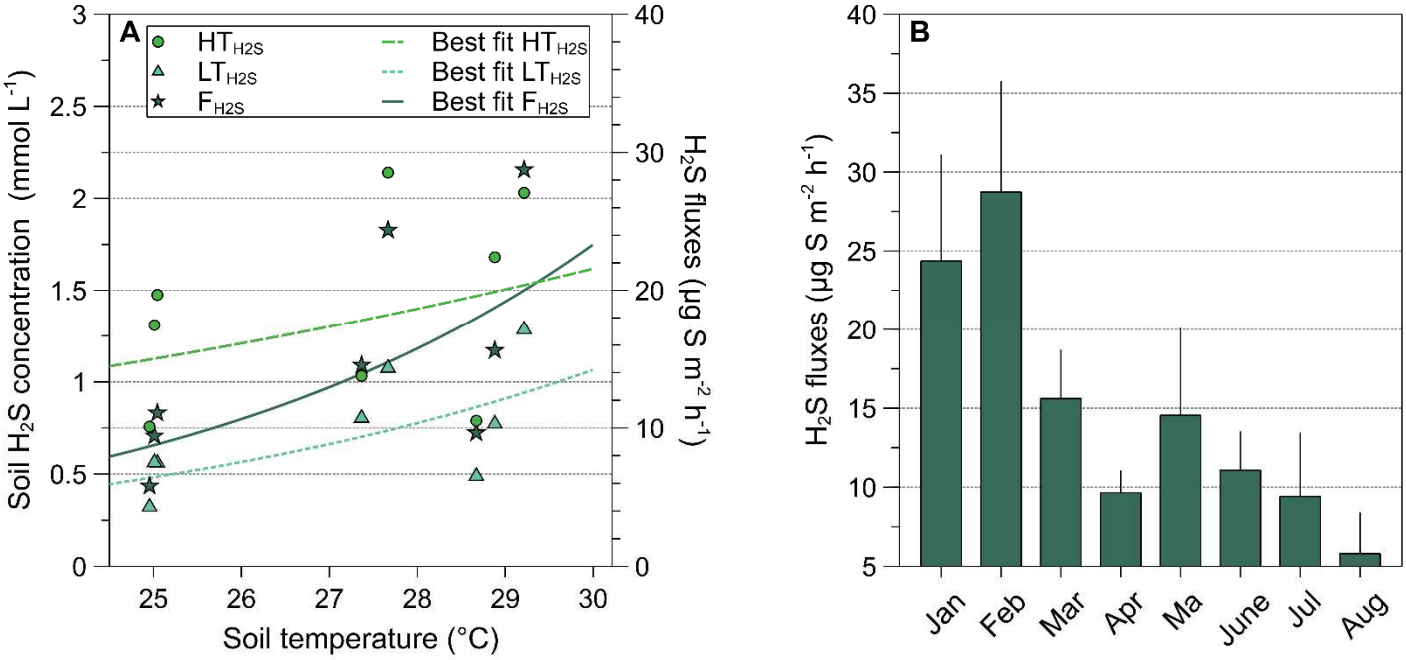

Fig. 1: A) Relationships between A) Monthly averages of soil H_2S concentrations and soil temperature (°C), and B) Soil-atmosphere H_2S fluxes (µg S m^{-2} h^{-1}) at low tide between January and August 2017. In the left panel, circles and triangles indicate high tide (HT) and low tide (LT) soil concentrations, respectively, while stars represent fluxes and lines are the best fit regressions with soil temperature.

Table 1: Soil H_2S concentrations (mmol L^{-1}) at low and high tide (mean ± SD) measured between January and August 2017

Months (2017)	January	February	March	April	May	June	July	August
Depth (cm)	*High tide*							
5	2.40 ± 0.59	2.01 ± 0.39	1.70 ± 0.53	0.73 ± 0.30	1.54 ± 0.14	1.24 ± 0.77	0.76 ± 0.51	0.34 ± 0.30
15	2.34 ± 0.57	2.39 ± 0.71	2.03 ± 0.94	0.56 ± 0.09	1.19 ± 0.14	1.76 ± 0.49	1.16 ± 1.07	0.59 ± 0.52
25	2.02 ± 0.66	1.67 ± 0.31	1.97 ± 0.64	0.77 ± 0.16	0.74 ± 0.59	1.40 ± 0.07	1.42 ± 0.27	0.73 ± 0.47
35	2.10 ± 0.33	2.10 ± 0.67	1.26 ± 0.72	0.9 ± 0.14	0.87 ± 0.29	1.39 ± 0.10	1.60 ± 0.41	1.09 ± 0.50
45	1.77 ± 0.50	2.27 ± 1.14	1.65 ± 0.92	0.83 ± 0.17	0.83 ± 0.29	1.53 ± 0.07	1.35 ± 0.57	0.99 ± 0.92
55	2.20 ± 0.21	1.73 ± 0.59	1.47 ± 0.37	0.94 ± 0.03	1.02 ± 0.27	1.53 ± 0.14	1.58 ± 0.3	0.80 ± 0.50
Depth (cm)	*Low tide*							
5	1.21 ± 0.14	1.44 ± 0.74	0.73 ± 0.13	0.44 ± 0.04	0.87 ± 0.21	0.51 ± 0.09	0.30 ± 0.10	0.16 ± 0.07
15	1.22 ± 0.33	1.43 ± 0.34	0.77 ± 0.16	0.47 ± 0.07	0.71 ± 0.27	0.54 ± 0.11	0.47 ± 0.20	0.29 ± 0.13
25	0.94 ± 0.11	1.17 ± 0.11	0.83 ± 0.29	0.47 ± 0.03	0.92 ± 0.19	0.54 ± 0.04	0.59 ± 0.10	0.27 ± 0.07
35	1.13 ± 0.19	1.23 ± 0.13	0.73 ± 0.41	0.50 ± 0.04	1.00 ± 0.20	0.59 ± 0.07	0.63 ± 0.03	0.47 ± 0.07
45	0.94 ± 0.30	1.27 ± 0.49	0.67 ± 0.26	0.50 ± 0.06	0.57 ± 0.09	0.59 ± 0.10	0.62 ± 0.09	0.37 ± 0.09
55	1.00 ± 0.09	1.16 ± 0.19	0.90 ± 0.13	0.54 ± 0.06	0.74 ± 0.20	0.59 ± 0.10	0.77 ± 0.03	0.37 ± 0.11

144

145 At low tide, the estimated average soil-atmosphere H_2S emission during the study period
146 was 14.90 ± 7.90 µg S m^{-2} h^{-1} (Fig. 1B). The largest emissions were measured in February with
147 28.74 ± 6.98 µg S m^{-2} h^{-1} and the smallest in August with 5.81 ± 2.58 µg S m^{-2} h^{-1}, consistent with the
148 seasonal variation in soil H_2S concentrations and temperature (Fig. 1A). However, it is possible that
149 these fluxes are over-estimated. At low tide, mangrove soils are covered with a biological membrane
150 composed of an assemblage of heterotrophic bacteria and autotrophic eukaryotes (Decho, 2000).
151 This biofilm has been shown to act as a physical barrier, reducing gas transfer at the soil-air interface
152 (see *e.g.* Jacotot *et al.*, 2019; Leopold *et al.*, 2013). In this study, theoretical fluxes were calculated

153 with the SAGM method, which does not account for a biofilm. As an indication, Jacotot *et al.* (2019)
154 noted an average increase of ~17% in CH_4 fluxes after removing the biofilm. To put these numbers
155 into perspective, we only found two studies of *in-situ* H_2S fluxes in mangrove forests, and they both
156 reported similar emissions to the present study, ranging from 3 to 31 µg S m^{-2} h^{-1} in Florida (Castro
157 and Dierberg 1987), and from 19 ± 5 to 51 ± 12 µg S m^{-2} h^{-1} in the Sundarbans (Ganguly *et al.* 2018).
158 By comparing these values to mangroves-associated ecosystems, such as saltmarshes, Delaune *et al.*
159 (2002) reported H_2S fluxes ranging from 5 to 79 µgS m^{-2} h^{-1}, which falls within the range of values
160 observed in mangroves and and supports this range of emission values. Nevertheless, the available
161 literature is currently insufficient to establish a plausible range of variation in H_2S emissions from
162 mangroves, as these may strongly differ in their physiographic characteristics. In addition, based on
163 our study, extrapolating to an average H_2S flux of the ecosystem is challenging because only low-tide
164 fluxes were estimated. However, to estimate average fluxes, emissions based on the tidal cycle
165 should be taken into account, as these ecosystems are submerged part of the time. Therefore, the
166 presence of an oxygenated water column can potentially offset surface fluxes, as H_2S can be oxidized
167 during its diffusion. Regardless, based on an average from the available data for mangroves, the
168 annual emissions would vary between 0.02 and 0.44 g S m^{-2}, which, compared with the 0.035 g S m^{-2}
169 reported by Yu *et al.* (2019) for coastal wetlands, would make mangroves potential hotspots of H_2S
170 emissions among coastal ecosystems.
171 In conclusion, this scoping study allowed for the determination of H_2S fluxes in a semi-arid
172 mangrove forest. The main important drivers of H_2S emissions identified herein were the soil H_2S
173 concentrations as well as seasonal temperature variability. The fluxes presented here were similar to
174 those reported by other studies, allowing furthering refining the global range of variation of H_2S
175 emissions from mangrove soils. A research effort should be performed to extend these measures to
176 other mangrove sites that differ in their physiographical conditions, but also to understand the
177 impact of local physicochemical parameters on H_2S emissions.
178

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References

Barton, L.L., Fardeau, M.-L., Fauque, G.D., 2014. Hydrogen Sulfide: A Toxic Gas Produced by Dissimilatory Sulfate and Sulfur Reduction and Consumed by Microbial Oxidation, in: Kroneck, P.M.H., Torres, M.E.S. (Eds.), The Metal-Driven Biogeochemistry of Gaseous Compounds in the Environment, Metal Ions in Life Sciences. Springer Netherlands, Dordrecht, pp. 237–277. https://doi.org/10.1007/978-94-017-9269-1_10

Bastviken, D., Cole, J., Pace, M., Tranvik, L., 2004. Methane emissions from lakes: Dependence of lake characteristics, two regional assessments, and a global estimate: LAKE METHANE EMISSIONS. Glob. Biogeochem. Cycles 18, n/a-n/a. https://doi.org/10.1029/2004GB002238

Castro, M.S., Dierberg, F.E., 1987. Biogenic hydrogen sulfide emissions from selected Florida wetlands. Water. Air. Soil Pollut. 33, 1–13.

Conant, R.T., Ryan, M.G., Ågren, G.I., Birge, H.E., Davidson, E.A., Eliasson, P.E., Evans, S.E., Frey, S.D., Giardina, C.P., Hopkins, F.M., Hyvönen, R., Kirschbaum, M.U.F., Lavallee, J.M., Leifeld, J., Parton, W.J., Megan Steinweg, J., Wallenstein, M.D., Martin Wetterstedt, J. å., Bradford, M.A., 2011. Temperature and soil organic matter decomposition rates - synthesis of current knowledge and a way forward. Glob. Change Biol. 17, 3392–3404. https://doi.org/10.1111/j.1365-2486.2011.02496.x

Davidson, E.A., Janssens, I.A., 2006. Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. Nature 440, 165–173. https://doi.org/10.1038/nature04514

Decho, A.W., 2000. Microbial biofilms in intertidal systems: an overview. Cont. Shelf Res. 17.

Delaune, R.D., Devai, I., Lindau, C.W., 2002. Flux of Reduced Sulfur Gases Along a Salinity Gradient in Louisiana Coastal Marshes. Estuar. Coast. Shelf Sci. 54, 1003–1011. https://doi.org/10.1006/ecss.2001.0871

Donato, D.C., Kauffman, J.B., Murdiyarso, D., Kurnianto, S., Stidham, M., Kanninen, M., 2011. Mangroves among the most carbon-rich forests in the tropics. Nat. Geosci. 4, 293–297. https://doi.org/10.1038/ngeo1123

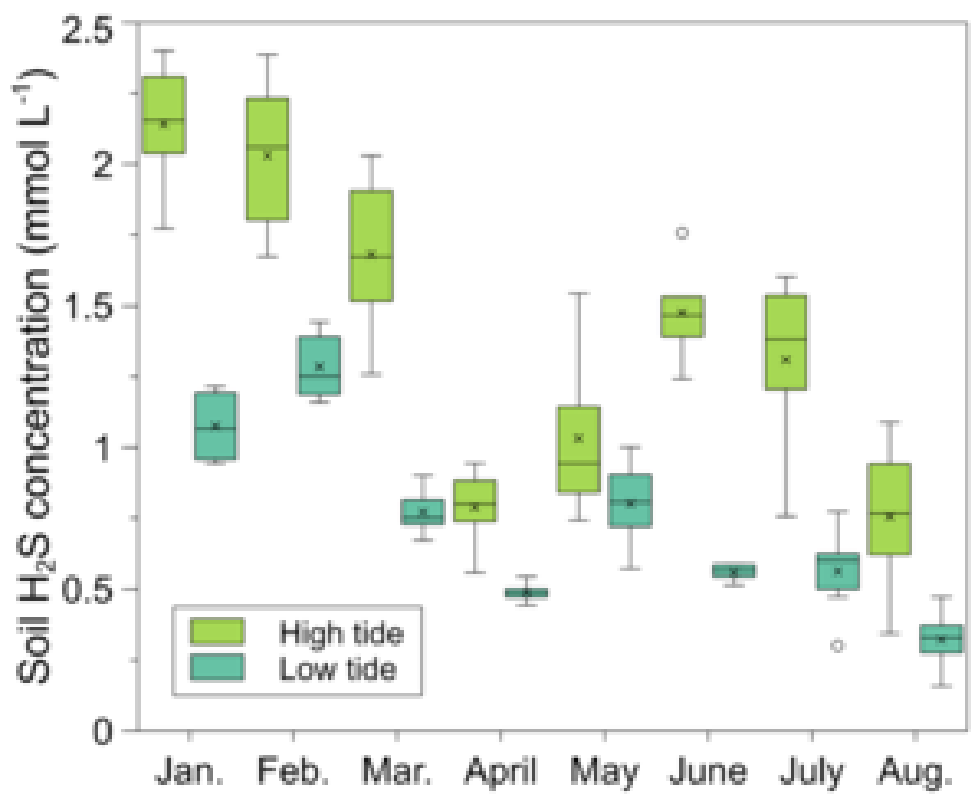
Ganguly, D., Ray, R., Majumdar, N., Chowdhury, C., Jana, T.K., 2018. Biogenic hydrogen sulphide emissions and non-sea sulfate aerosols over the Indian Sundarban mangrove forest. J. Atmospheric Chem. 75, 319–333. https://doi.org/10.1007/s10874-018-9382-3

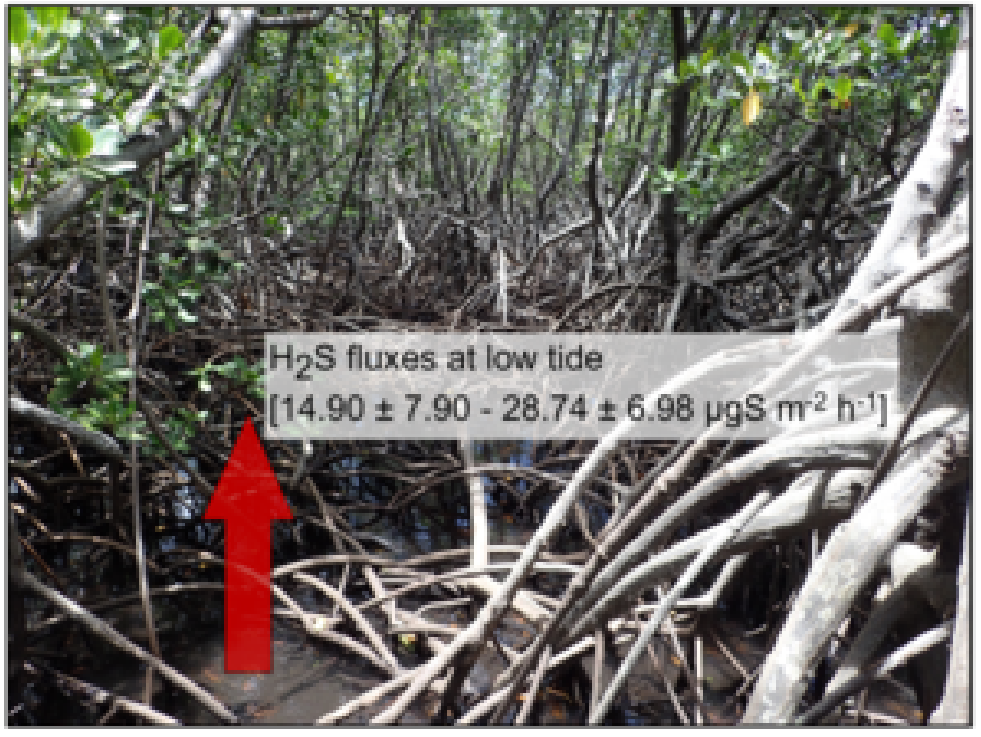
Jacotot, A., Marchand, C., Allenbach, M., 2019. Biofilm and temperature controls on greenhouse gas (CO2 and CH4) emissions from a Rhizophora mangrove soil (New Caledonia). Sci. Total Environ. 650, 1019–1028. https://doi.org/10.1016/j.scitotenv.2018.09.093

Kristensen, E., Bouillon, S., Dittmar, T., Marchand, C., 2008. Organic carbon dynamics in mangrove ecosystems: A review. Aquat. Bot. 89, 201–219. https://doi.org/10.1016/j.aquabot.2007.12.005

Kristensen, E., Connolly, R.M., Otero, X.L., Marchand, C., Ferreira, T.O., Rivera-Monroy, V.H., 2017. Biogeochemical Cycles: Global Approaches and Perspectives, in: Rivera-Monroy, V.H., Lee, S.Y., Kristensen, E., Twilley, R.R. (Eds.), Mangrove Ecosystems: A Global Biogeographic

Perspective. Springer International Publishing, Cham, pp. 163–209. https://doi.org/10.1007/978-3-319-62206-4_6
Lee, R.Y., Porubsky, W.P., Feller, I.C., McKee, K.L., Joye, S.B., 2008. Porewater biogeochemistry and soil metabolism in dwarf red mangrove habitats (Twin Cays, Belize). Biogeochemistry 87, 181–198. https://doi.org/10.1007/s10533-008-9176-9
Leopold, A., Marchand, C., Deborde, J., Chaduteau, C., Allenbach, M., 2013. Influence of mangrove zonation on CO2 fluxes at the sediment–air interface (New Caledonia). Geoderma 202–203, 62–70. https://doi.org/10.1016/j.geoderma.2013.03.008
Sander, R., 1999. Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry (Version 3).
Watts, S.F., 2000. The mass budgets of carbonyl sulfide, dimethyl sulfide, carbon disulfide and hydrogen sulfide. Atmos. Environ. 34, 761–779. https://doi.org/10.1016/S1352-2310(99)00342-8
Yu, Q., Si, G., Zong, T., Mulder, J., Duan, L., 2019. High hydrogen sulfide emissions from subtropical forest soils based on field measurements in south China. Sci. Total Environ. 651, 1302–1309. https://doi.org/10.1016/j.scitotenv.2018.09.301


Soil H_2S concentration (mmol L^{-1})
2.5
2
1.5
1
0.5
0
High tide
Low tide
Jan.
Feb.
Mar.
April
May
June
July
Aug.


H_2S fluxes at low tide
[14.90 ± 7.90 - 28.74 ± 6.98 µgS m^{-2} h^{-1}]