

Nitrous oxide and methane emissions from the restored mangrove ecosystem of the Ciénaga Grande de Santa Marta, Colombia



Dennis Konnerup^{a,*}, Julián Mauricio Betancourt-Portela^b, Carlos Villamil^b,
Juan Pablo Parra^b

^aSchool of Plant Biology, The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia

^bInstituto de Investigaciones Marinas y Costeras (INVEMAR), Playa Salguero, El Rodadero, Santa Marta, Colombia

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ABSTRACT

Most studies on emission of the greenhouse gases nitrous oxide (N₂O) and methane (CH₄) have been carried out in temperate areas so there is generally a lack of data from subtropical and tropical climates. A large part of the subtropical and tropical coastal wetlands consists of mangrove ecosystems, which have potential to act as sources of N₂O and CH₄. We measured N₂O and CH₄ emissions during 11 months in the brackish lagoon system Ciénaga Grande de Santa Marta (CGSM) on the Caribbean coast of Colombia. The area has been seriously influenced by human disturbance which resulted in approximately 60% mangrove mortality but the ecosystem is now being rehabilitated. In addition to N₂O and CH₄ emissions at four sampling sites, we also measured temperature, salinity, pH, dissolved oxygen (DO), redox potential, nitrite (NO₂⁻), nitrate (NO₃⁻), ammonium (NH₄⁺) and organic material in the water and/or the sediment.

We found the mangrove sediments of CGSM to be a source of N₂O and CH₄ but there was large variability of the emissions on both temporal and spatial scale with N₂O and CH₄ fluxes in the range 35–1180 μg m⁻² h⁻¹ and 0–31570 μg m⁻² h⁻¹, respectively. Correlations between N₂O fluxes and the water variables showed that salinity significantly contributed towards decreased emission of N₂O ($r = -0.38$). By contrast, water concentrations of NO₃⁻ were correlated with increased emission of N₂O ($r = 0.54$). Emission of CH₄ was negatively correlated with DO in the water ($r = -0.34$) and there was a positive correlation between organic matter and CH₄ emission ($r = 0.75$). It was found that untreated wastewater discharged into the Magdalena River and in turn, the lagoon system may have resulted in a substantially higher emission of both N₂O and CH₄ as the wastewater contributes substrate to the processes in the form of N and organic matter. With better treatment of wastewater, it is possible that emission of both gases would be lower, especially at the sites closest to Magdalena River.

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1. Introduction

Nitrous oxide (N₂O) and methane (CH₄) are important trace gases in the atmosphere contributing to global warming. Concentrations of both N₂O and CH₄ have increased steadily since the beginning of industrial times. This is a major concern and contributes significantly to global climate change since both gases although present in lower concentrations to that of CO₂, have 296 (N₂O) and 23 (CH₄) times the global warming potential of CO₂ (IPCC, 2001). Recent estimates suggest that N₂O and CH₄ contribute approximately 20% and 6%, respectively, of the global warming

effect caused by the various greenhouse gases. Almost one-third of CH₄ emissions are from natural sources such as wetlands and lakes, whereas 55% of the total global N₂O emissions are from natural ecosystems (IPCC, 2001; Forster et al., 2007). However, most wetland studies have been carried out in temperate areas and there is generally a lack of estimates of N₂O and CH₄ fluxes from subtropical and tropical climates.

A large part of subtropical and tropical coastal wetlands consists of mangrove ecosystems, which are located in the intertidal zone of estuaries, bays, gulfs and part of the riparian zone (Alongi, 2002). The distribution of mangroves occurs across highly dynamic environmental gradients like salinity, temperature, oxygen, redox potential and different nutrient input from the surroundings (Tam and Wong, 1998; Clark et al., 1998; Gleason et al., 2003; Marchand et al., 2004). The sediment characteristics of mangrove ecosystems also

* Corresponding author.

E-mail address: dennis.konnerup@uwa.edu.au (D. Konnerup).

differ from coarse sand to black fine estuary mud and this results in different abiotic and biotic conditions between mangrove areas (Alongi et al., 2005). These differences influence the microbial processes which regulate the fluxes of N_2O and CH_4 (Bauza et al., 2002; Whalen, 2005). Mangrove sediments can act as sources of the two gases and it has been shown that the emission of CH_4 can have a large variation with over 3 orders of magnitude, from about $3 \mu g m^{-2} h^{-1}$ to $44 mg m^{-2} h^{-1}$ (Barnes et al., 2006; Dalal et al., 2008; Dalal and Allen, 2008).

The Caribbean lagoon system Ciénaga Grande de Santa Marta (CGSM) in northern Colombia is Colombia's largest coastal lagoon system (Fig. 1). The area has been seriously affected by human disturbance, beginning with the construction of a highway along the northern part of the lagoon in the 1950s, which changed the hydrology and obstructed the natural water flow through the lagoon system (Botero and Mancera, 1996). Freshwater flow from the Magdalena River was also reduced by closing of channels and the hydrological changes led to a severe increase in salinity because evaporation in the area is more than twice as high as the rainfall. As a result of these changes, about 30,000 ha of the original 51,150 ha mangrove forest died (González, 1991). Subsequent eutrophication and decreased fish populations had severe socioeconomic consequences for the area. Since 1978, different steps have been made to restore the ecosystem which included the aim of reestablishing the original hydrological conditions to the area. Installation of box culverts at different points under the highway in 1989 allowed water exchange to the Caribbean Sea. Another step involved opening of channels from Magdalena River to reestablish the original flow of freshwater to the lagoon system. This has been done in several steps and the last channels were opened in the late 1990s (Perdomo et al., 1998; Elster et al., 1999). However, as it was not enough just to reestablish the original water flow to rehabilitate the area, projects with reforestation of mangroves by propagules, seedlings and saplings were also carried out (Elster, 2000).

In the present study the aim was to quantify the emission of the greenhouse gases N_2O and CH_4 at four different areas in which the

mangrove vegetation had been affected by the hypersalinization to different extent and to correlate the emissions with water and sediment characteristics to determine which factors are controlling the fluxes of N_2O and CH_4 in this mangrove ecosystem.

2. Materials and methods

2.1. Site description

The study was carried out in the coastal lagoon system Ciénaga Grande de Santa Marta which extends from the foot of the Sierra Nevada de Santa Marta to Magdalena River ($10^{\circ}35'$ and $11^{\circ}01'N$; $74^{\circ}16'$ and $74^{\circ}44'W$) in the north of Colombia. The climate in the area is characterized as dry tropical with a mean temperature of $28^{\circ}C$ and the precipitation is ca. 700 mm per year with most of the rain falling between July and November (IGAC, 1973). The hydrology of the lagoon system is mainly influenced by the freshwater supply of several rivers and the changes between rainy and dry season. The water level changes ca. 0.5 m between the seasons and influence of the tide is negligible (Elster, 2000).

2.2. Sampling stations

The four study sites were selected according to the conservation status of the mangrove (Fig. 1). The mangrove stands are composed mainly of *Avicennia germinans* (L.) Stearn, *Laguncularia racemosa* (L.) Gaertn. f., and *Rhizophora mangle* L. At open sites *Batis maritima* L. and *Sesuvium portulacastrum* L. can cover large areas. The four zones each represented a degree of conservation status with the following characteristics:

Station Rinconada ($10^{\circ} 57' 41.4''N$; $74^{\circ} 29' 37.6''W$) represents a zone with a relatively good conservation status. The vegetation consists mainly of *Rhizophora mangle* and *Avicennia germinans* with heights in the range 5–7 m.

Station Caño Dragado ($10^{\circ} 55' 40.2''N$; $74^{\circ} 34' 42.4''W$) is considered as the zone with highest disturbance. The mangrove

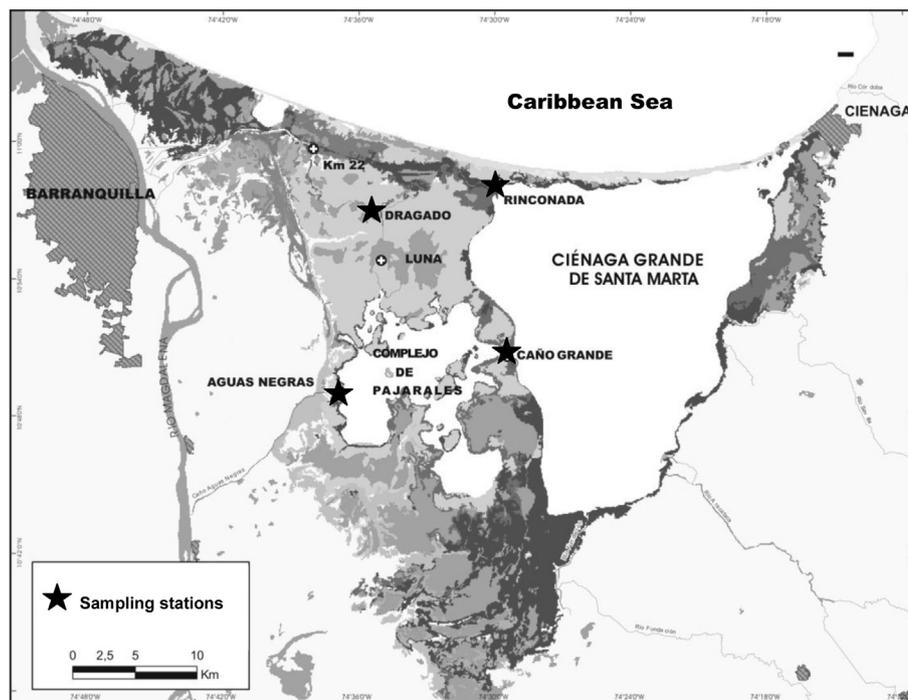


Fig. 1. Map of the lagoon system Ciénaga Grande de Santa Marta in northern Colombia. The four sampling stations in the study are marked with stars: Aguas Negras, Caño Dragado, Caño Grande and Rinconada.

trees died in this area because of the hypersalinization of the soil and the mangrove vegetation disappeared completely with only the dead trunks left behind.

Station Caño Grande (10° 51' 42.8"N; 74° 28' 52.9"W) is a zone in the process of rehabilitation mediated by planting of seedlings since 2000.

Station Aguas Negras (10° 48' 32.2"N; 74° 36' 26.9"W) This station represents a mangrove forest in the process of natural regeneration after the opening of the channel Aguas Negras allows freshwater from Magdalena River to enter the area.

2.3. Experimental design

The sampling campaigns were conducted during 11 months from June 2005 to May 2006 to cover both the dry season and the rainy season. Measurements of fluxes of N₂O and CH₄ from the sediment were conducted at each sampling station monthly between 10.00 and 16.00 h. Furthermore, water and sediment samples were also collected to determine environmental variables and water quality.

2.4. Measurements of sediment gas fluxes

The closed chamber method was used to quantify the fluxes of gases across the sediment-atmosphere or water–atmosphere interfaces depending on the water level at the time of measurement. The measurements were taken using chambers made of PVC pipe (Allen et al., 2007). Each gas measurement campaign consisted of four chambers set up randomly at each sampling station. Chambers were carefully inserted ca. 5 cm into the sediment to ensure minimal lateral gas leakage. Prior to sampling, the chambers were left open for approximately 20 min to minimize disturbance effects of the soil surface caused by the insertion of the chambers. The chambers were then sealed with lids and gas samples were taken through a septum in the lid. Gas samples were taken with a syringe at intervals of 3 min from 0 to 9 min and were stored in pre-evacuated vials before they were cooled and transported to the laboratory where they were analyzed for concentrations of N₂O and CH₄. The temperature inside the chamber at each sampling was recorded using a needle-like thermometer, which was inserted in the chamber through a septum in the lid. The gas concentrations were corrected for temperature and atmospheric pressure at the time of sampling.

The samples were analyzed by a gas chromatograph (Shimadzu GC14A, Kyoto, Japan) with 2 columns for analysis of CH₄ and N₂O concentrations using N₂ as a carrier gas. Gas concentrations were quantified by comparing areas for samples and standards. For this purpose, calibration gas samples were used as gas standards with 1–3 ppm N₂O and CH₄.

Fluxes were calculated using linear fit of the time series of gas concentrations and increases of N₂O and CH₄ fluxes over the incubation period were linear ($R^2 > 0.95$). Occasionally, outlying data points were omitted in the time series if the sample at 0 min showed concentrations substantially different from the concentration in the ambient air. Less than 10% of the data were omitted because of this criterion.

2.5. Measurements of environmental variables

At the monthly gas samplings, standing water around or within a few meters from the chambers was analyzed for salinity (Practical Salinity Scale) with an electrical conductivity meter connected to a portable multimeter (WTW-320, Weilheim, Germany), pH was measured with a glass electrode connected to the same multimeter and dissolved oxygen (DO) was measured with an electrode

Table 1

Water quality variables (Mean ± SD) at four different sampling stations (Aguas Negras, Caño Dragado, Caño Grande and Rinconada) in the mangroves of the Ciénaga Grande de Santa Marta, Colombia in rainy and dry season.

	Season	Aguas Negras	Caño Dragado	Caño Grande	Rinconada
Temperature (°C)	Rainy	30.6 ± 2.1	35.7 ± 2.9	32.8 ± 3.2	31.6 ± 3.7
	Dry	32.0 ± 4.0	32.1 ± 2.5	32.4 ± 4.7	31.2 ± 3.3
DO (mg l ⁻¹)	Rainy	2.4 ± 2.4 ^a	9.3 ± 2.0 ^b	5.4 ± 2.4 ^{ab}	3.7 ± 2.7 ^a
	Dry	3.6 ± 2.5	6.0 ± 1.1 [*]	4.8 ± 2.8	5.1 ± 3.7
pH	Rainy	7.2 ± 0.5 ^a	8.5 ± 0.2 ^b	8.0 ± 0.8 ^{ab}	7.7 ± 0.7 ^{ab}
	Dry	7.5 ± 0.7 ^a	8.3 ± 0.2 ^{ab}	8.0 ± 0.4 ^{ab}	8.1 ± 0.3 ^{ab}
Salinity	Rainy	2.7 ± 1.9 ^a	23.4 ± 5.7 ^b	14.1 ± 5.7 ^b	14.4 ± 7.0 ^b
	Dry	2.7 ± 2.5	12.3 ± 15.3	11.5 ± 6.7	18.9 ± 6.8
NO ₂ ⁻ (µg l ⁻¹)	Rainy	4.1 ± 3.9	4.0 ± 2.7	4.5 ± 3.8	4.0 ± 3.4
	Dry	2.7 ± 1.0 ^{ab}	3.6 ± 1.0 ^b	2.3 ± 0.8 ^a	3.1 ± 0.6 ^{ab}
NO ₃ ⁻ (µg l ⁻¹)	Rainy	5.0 ± 4.0	4.0 ± 1.7	6.1 ± 1.2	3.5 ± 2.2
	Dry	28.6 ± 27.5 ^b	2.9 ± 2.6 ^a	4.4 ± 3.6 ^a	6.0 ± 6.3 ^{ab}
NH ₄ ⁺ (µg l ⁻¹)	Rainy	27.7 ± 16.6	46.7 ± 59.7	14.5 ± 11.6	21.8 ± 17.1
	Dry	66.3 ± 57.7	123.6 ± 144.4	52.4 ± 58.3	58.0 ± 71.1

Different letters indicate significant difference between stations and * indicates difference between season at a given sampling station ($P < 0.05$).

connected to another portable DO meter (WTW-330, Weilheim, Germany). In the sediment, salinity and pH were also measured as well as redox potential (Eh) using a platinum electrode and an Ag/AgCl reference electrode connected to a multimeter (WTW-320, Weilheim, Germany).

At the beginning of the study, samples of surface sediment were collected from each station for a detailed characterization. Sediment from the top layer (5 cm) was sampled with a spatula and stored cooled until arrival at the laboratory. The samples were analyzed for nutrient concentrations, content of organic material and particle size. Percentage of mud was defined as sediment size <0.0625 mm diameter (Dennison and Abal, 1999).

In both water and sediment samples inorganic nitrogen (N) concentrations (NH₄⁺, NO₃⁻ and NO₂⁻) were determined according to standard methods (APHA, 1998). Sediment samples were measured after extraction with 1 M KCl. Content of organic material was determined by ignition at 500 °C.

2.6. Conversion to CO₂ equivalents

To compare the impact of the greenhouse gases, fluxes of N₂O and CH₄ were converted to CO₂ equivalents (CO₂-e). Conversion factors of 296 for N₂O and 23 for CH₄ were used to calculate global warming potential in CO₂-e (IPCC, 2001).

2.7. Statistical analyses

The data were classified as collected in either the dry season or the rainy season. The dry season was defined as the period from December to June and rainy season from July to November. Data were analyzed by analysis of variance (ANOVA) using the software Statgraphics XV centurion version 15.1.02 (Statpoint, Inc., USA) to find statistical differences between stations and season. The level of significance was 0.05 in all cases. All data were tested for normal distribution by Kolmogorov–Smirnov test and for homogeneity of variance by Bartlett's test. If necessary, logarithmic or square root transformations were performed to ensure homogeneity of variance, but for clarity all data are presented as untransformed. Multiple comparisons of means were performed using Tukey HSD procedure.

3. Results

3.1. Water variables

Water temperatures were relatively stable with mean values in the range 30.6–35.7 °C and no statistical differences among stations or seasons (Table 1). However, DO concentrations were significantly different among stations in the rainy season with the highest mean at Caño Dragado and the lowest at Aguas Negras. The mean pH values were significantly lower at Aguas Negras compared to Caño Dragado in both rainy and dry seasons, but overall pH means were quite stable in the range 7.2–8.5. Water salinity showed clear differences among stations in the rainy season, with lowest concentrations at Aguas Negras and highest at Caño Dragado. However, the variation in salinity is shown more clearly when plotted month by month (Fig. 2). Water salinities at all stations were highest at the end of the dry season and decreased during the rainy season, until they started to increase again when the dry season began in December.

Oxidized N in the form of NO_2^- and NO_3^- were found in low concentrations at all stations in the rainy season, with mean concentrations in the range 3.5–6.0 $\mu\text{g l}^{-1}$. However, in the dry season there was a significant difference in NO_3^- concentrations among stations, with Aguas Negras having the highest concentration at a mean of 28.6 $\mu\text{g l}^{-1}$. Concentrations of NH_4^+ were in the range 14.5–123.6 $\mu\text{g l}^{-1}$ with high variability and there were neither significant differences among stations, nor seasons.

3.2. Sediment variables

Sediment salinities were significantly different among stations in the rainy season but not in the dry season (Table 2). As with the water salinities it was shown that salinities tended to be highest at the end of the dry season and then decreased during the rainy season as the salt was flushed out of the sediment (Fig. 2). However, this pattern is less clear with the sediment salinities compared to the water salinities. Redox potentials were in the range from –308 to –47 mV and there were no differences among stations or seasons. Likewise, the N forms NH_4^+ , NO_3^- and NO_2^- did not show significant differences among stations or seasons. The percentage of mud in the sediment differed among stations being highest at Rinconada with 77.1% and lowest at Caño Dragado with 19.1%. The contents of organic material were also significantly different among stations with the highest content of 53.2% at Caño Dragado and the other stations were in the range 17.8–29.8%.

3.3. N_2O and CH_4 fluxes from mangrove sediments

Positive fluxes of N_2O were recorded at all sites during all months and were ranging from 35 to 1180 $\mu\text{g m}^{-2} \text{h}^{-1}$ (Fig. 3). The N_2O fluxes differed significantly among the four mangrove stations in both rainy and dry season being highest at Aguas Negras with mean fluxes of 747 and 931 $\mu\text{g m}^{-2} \text{h}^{-1}$ in the rainy and dry season, respectively (Table 3).

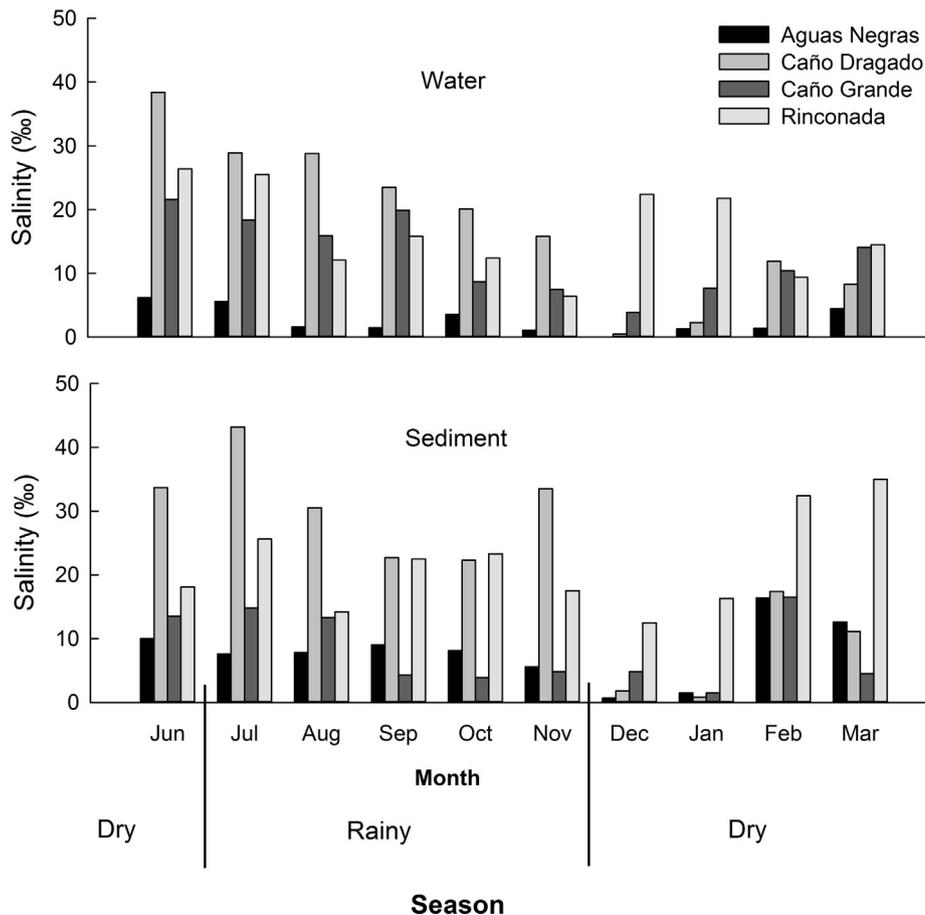


Fig. 2. Salinity of water and sediment porewater at four sampling stations: Aguas Negras, Caño Dragado, Caño Grande and Rinconada in the lagoon system Ciénaga Grande de Santa Marta, Colombia during 10 months covering both rainy and dry season.

Table 2

Sediment variables (Mean \pm SD) at four different sampling stations (Aguas Negras, Caño Dragado, Caño Grande and Rinconada) in the mangroves of the Ciénaga Grande de Santa Marta, Colombia in rainy and dry season.

	Season	Aguas Negras	Caño Dragado	Caño Grande	Rinconada
pH	Rainy	6.8 \pm 0.4 ^a	7.1 \pm 0.1 ^{ab}	7.6 \pm 0.4 ^b	7.4 \pm 0.4 ^{ab}
	Dry	6.4 \pm 0.8	7.1 \pm 0.3	7.1 \pm 0.2	6.4 \pm 1.3
Salinity	Rainy	7.6 \pm 1.2 ^a	30.4 \pm 8.6 ^b	8.2 \pm 5.4 ^a	20.6 \pm 4.6 ^b
	Dry	8.2 \pm 6.9	13.0 \pm 13.5 [*]	8.2 \pm 6.5	22.9 \pm 10.1
Eh (mV)	Rainy	-161.7 \pm 48.0	-307.7 \pm 57.7	-221.3 \pm 53.3	-302.0 \pm 135.7
	Dry	-127.8 \pm 94.6	-193.3 \pm 135.0	-208.1 \pm 85.5	-47.3 \pm 35.1
NO ₂ ⁻ (μ g g ⁻¹)	Rainy	4.5 \pm 2.8	4.7 \pm 3.2	4.8 \pm 5.3	5.0 \pm 5.5
	Dry	4.8 \pm 2.2	5.2 \pm 3.5	3.3 \pm 2.5	4.4 \pm 1.9
NO ₃ ⁻ (μ g g ⁻¹)	Rainy	32.3 \pm 28.5	24.8 \pm 32.2	5.4 \pm 4.3	5.2 \pm 4.3
	Dry	15.2 \pm 10.6	10.7 \pm 12.1	10.1 \pm 11.8	3.9 \pm 4.6
NH ₄ ⁺ (μ g g ⁻¹)	Rainy	75.7 \pm 68.9	82.6 \pm 98.0	42.4 \pm 59.0	31.4 \pm 45.3
	Dry	134.3 \pm 89.2	154.3 \pm 271.5	99.4 \pm 138.7	92.8 \pm 133.3
% Mud		50.8 \pm 16.4 ^b	19.1 \pm 5.0 ^a	38.8 \pm 12.0 ^{ab}	77.1 \pm 7.1 ^c
% Organic material		29.8 \pm 5.0 ^a	53.2 \pm 7.8 ^b	17.8 \pm 0.3 ^a	22.4 \pm 0.4 ^a

Different letters indicate significant difference between stations and * indicates difference between season at a given sampling station ($P < 0.05$).

Fluxes of CH₄ showed high variation and were in the range from not detectable to 31,570 μ g m⁻² h⁻¹ (Fig. 3). There was no significant difference among stations in the rainy season although the mean of Caño Dragado was 425 μ g m⁻² h⁻¹ and the mean of Caño Grande was 6925 μ g m⁻² h⁻¹ i.e. 16 times higher but with large standard deviations (Table 3). In the dry season there was significant difference among stations with Caño Grande having the highest CH₄ flux of 11,781 μ g m⁻² h⁻¹ and Caño Dragado the lowest flux of 107 μ g m⁻² h⁻¹.

Correlations between N₂O fluxes and the water variables showed that salinity significantly contributed towards decreased

emission of N₂O ($r = -0.38$, Table 4). By contrast, water concentrations of NO₃⁻ were correlated with increased emission of N₂O ($r = 0.54$). Emission of CH₄ was negatively correlated with DO in the water ($r = -0.34$). In the sediment there was found a positive correlation between organic matter and CH₄ emission ($R = 0.75$).

When N₂O and CH₄ emissions were expressed as CO₂ equivalents, the values were in the range 41.5–838.0 mg m⁻² h⁻¹ and the seasonal means were in the range 122.4–361.9 mg m⁻² h⁻¹ with significant difference among stations in rainy but different in the dry season (Table 5). There was also a significant difference in how much of the CO₂ equivalents that could be attributed to N₂O

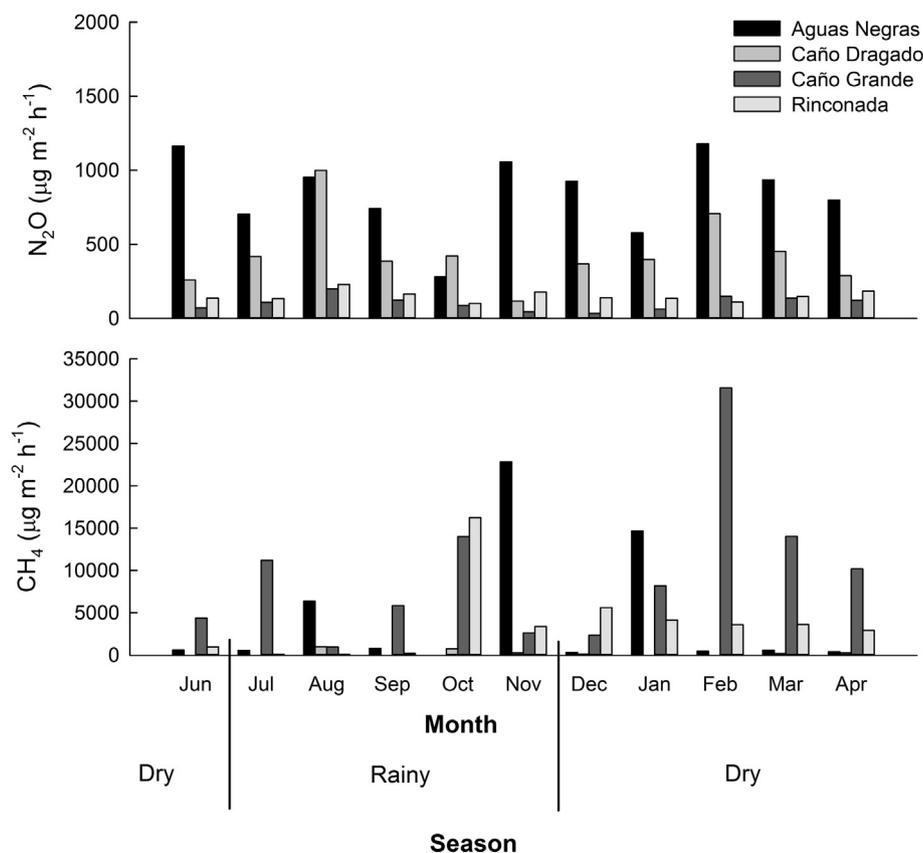


Fig. 3. Fluxes of N₂O and CH₄ from mangrove sediment at four sampling stations: Aguas Negras, Caño Dragado, Caño Grande and Rinconada in the lagoon system Ciénaga Grande de Santa Marta, Colombia during 11 months covering both rainy and dry season.

Table 3
Emissions of CH₄ and N₂O (Mean ± SD) at four different sampling stations (Aguas Negras, Caño Dragado, Caño Grande and Rinconada) in the mangroves of the Ciénaga Grande de Santa Marta, Colombia in rainy and dry season.

	Season	Aguas Negras	Caño Dragado	Caño Grande	Rinconada
N ₂ O (μg m ⁻² h ⁻¹)	Rainy	747 ± 299 ^b	469 ± 322 ^{ab}	114 ± 57 ^a	162 ± 48 ^a
	Dry	931 ± 227 ^c	413 ± 161 ^b	97 ± 46 ^a	144 ± 24 ^a
CH ₄ (μg m ⁻² h ⁻¹)	Rainy	6116 ± 9692	425 ± 421	6925 ± 5556	3999 ± 6984
	Dry	2838 ± 5795 ^{ab}	107 ± 102 ^a	11,781 ± 10,545 ^b	3474 ± 1525 ^{ab}

Different letters indicate significant difference between stations ($P < 0.05$).

Table 4
Regression analysis with correlation coefficients (r values) of N₂O and CH₄ emissions in the mangroves of the Ciénaga Grande de Santa Marta, Colombia and variables in water and sediment.

	Variable	N ₂ O	CH ₄
Water	Temperature	-0.10	-0.19
	DO	-0.15	-0.34*
	pH	-0.25	-0.24
	Salinity	-0.38*	-0.16
	Nitrite	-0.10	-0.40
	Nitrate	0.54*	-0.17
	Ammonium	0.03	-0.24
Sediment	pH	-0.12	0.19
	Salinity	-0.14	-0.21
	Eh	0.04	-0.03
	Nitrite	-0.10	-0.17
	Nitrate	0.11	-0.09
	Ammonium	-0.33	0.22
	% Mud	-0.20	-0.30
	% Organic material	-0.46	0.75*

Significant correlations are marked with * ($P < 0.05$).

emission. At Aguas Negras and Caño Dragado, N₂O contributed 77.9–97.6% of the CO₂ equivalents whereas Caño Grande had the lowest contribution of N₂O with 26.3% and 12.2% in the rainy and dry season, respectively.

4. Discussion

This study demonstrates that tropical mangrove sediments from anthropogenically disturbed sites in the Caribbean region of Colombia are a source of both N₂O and CH₄. However, there were large temporal and spatial variations for both gases suggesting that the variables controlling the emission are complex. Although there was a large variation in the emission, it was still possible to observe a pattern with differences among the four stations. Emissions of N₂O were highest at Aguas Negras which is the station closest to the Magdalena River with rates up to 1180 μg m⁻² h⁻¹ whereas Rinconada and Caño Grande had substantially lower rates in the range 35–230 μg m⁻² h⁻¹. The high emission at Aguas Negras could be due to N inputs from the Magdalena River since there is a high discharge of wastewater from cities and towns along the river (Restrepo et al., 2006). Studies from mangrove ecosystems in the tropical and subtropical regions of Australia have suggested that

mangrove systems have potential to be a large source of CH₄ while large emissions of N₂O have mainly been observed in tropical forest and agricultural systems (Dalal and Allen, 2008). However, it is possible that mangrove systems under particular conditions can act as 'hotspots' for N₂O emissions, especially when large amounts of N are present (Allen et al., 2011). This was also demonstrated by Corredor et al. (1999) who found N₂O emission rates up to 343 μg m⁻² h⁻¹ in a mangrove area in Puerto Rico that received a substantial nutrient input from guano. The rates in the present study are even higher with rates up to 1180 μg m⁻² h⁻¹ and are comparable to the ones found at agricultural systems with sugarcane (Allen et al., 2011). We found a strong positive correlation between NO₃⁻ in the water and emission of N₂O which further indicates that the high N₂O emissions could be explained by input of untreated wastewater from the surroundings since concentrations of NO₃⁻ were highest at Aguas Negras.

Emissions of CH₄ also varied considerably by fluxes between 0 and 31.6 mg m⁻² h⁻¹ with the highest emission at Caño Grande and the lowest at Caño Dragado. Studies from Australian wetlands including mangroves have also shown a wide range in CH₄ emissions varying from 3 μg m⁻² h⁻¹ to 44 mg m⁻² h⁻¹ (Dalal and Allen, 2008; Dalal et al., 2008) whereas a study in two Tanzanian mangrove forests found CH₄ emission rates in the range 7–234 μg m⁻² h⁻¹ (Kristensen et al., 2008). The high variation in emission of both N₂O and CH₄ in this and other studies reflects the high variability in spatial and temporal factors controlling the emissions in mangroves. This is probably because mangrove areas are influenced by small scale processes (e.g. diurnal and seasonal variation and sediment characteristics) as well as long-term climate patterns and estuarine mixing (Barnes et al., 2006; Romigh et al., 2006; Allen et al., 2011). Most of the methane emission studies to date have been in peatlands (bogs and fens) and freshwater marshes (Mitsch et al., 2010). Hadi et al. (2005) measured methane emissions from tropical peatlands in Indonesia and found rates of 0.37–1.65 mg m⁻² h⁻¹, with the highest number from cultivated paddy fields. Delaune and Pezeshki (2003) reported methane emissions of 0.2–18.7 mg m⁻² h⁻¹ in subtropical Louisiana freshwater marshes with the greatest methane emissions occurring in the summer months. In western Costa Rica, a seasonally flooded, tropical wetland had an average CH₄ emission of 33.7 mg m⁻² h⁻¹ which was significantly higher than averages of 3.74 and 8.67 mg m⁻² h⁻¹ measured in two other wetlands in eastern Costa

Table 5
Emissions of CH₄ and N₂O calculated as CO₂ equivalents (Mean ± SD), percent N₂O contribution (Mean ± SD) and range of N₂O contribution at four different sampling stations (Aguas Negras, Caño Dragado, Caño Grande and Rinconada) in the mangroves of the Ciénaga Grande de Santa Marta, Colombia in rainy and dry season.

	Season	Aguas Negras	Caño Dragado	Caño Grande	Rinconada
CO ₂ -eq (mg m ⁻² h ⁻¹)	Rainy	361.9 ± 293.1	148.7 ± 102.4	193.0 ± 123.1	140.0 ± 151.3
	Dry	340.7 ± 93.8 ^b	124.8 ± 46.5 ^a	299.7 ± 253.8 ^b	122.4 ± 34.9 ^a
% N ₂ O	Rainy	77.9 ± 26.2 ^b	92.6 ± 6.5 ^b	26.3 ± 26.7 ^a	66.2 ± 40.3 ^{ab}
	Dry	86 ± 25.6 ^c	97.6 ± 2.4 ^c	12.2 ± 4.4 ^a	37.8 ± 14.9 ^b
% N ₂ O range	Rainy	37.3–100.0	84.5–99.1	7.6–73.0	7.5–97.1
	Dry	33.7–97.4	93.5–100.0	5.8–17.7	24.4–64.7

Different letters indicate significant difference between stations ($P < 0.05$).

Rica in an area that is more humid and less affected by season (Mitsch et al., 2010). These data suggest that wetlands with pulsing hydrology may have higher CH₄ emissions than those wetlands that are continuously wet. In the present study we did not find differences in emissions of the two gases between dry and rainy season. Some studies have shown significantly different emissions of N₂O and CH₄ in dry and rainy season with positive correlations between emissions and temperature (Barnes et al., 2006; Krupadam et al., 2007). The water temperatures in our study were a little above 30 °C and fairly constant throughout the year with no difference between dry and rainy season which possibly can be some of the reason why we did not observe seasonal variation in gas emissions. However, seasonal variation in emissions can also be attributed to interactive effects of seasonal rainfall with temperature, humidity, evaporative rates, freshwater input and tidal hydrology (Eyre et al., 1998; Allen et al., 2011). Higher tidal water level and increased rainfall from seasonal rain can result in decreased porewater salinity, increased oxygen and nutrient availability and changes in CH₄ oxidation because of increased oxygen availability at the sediment surface (Dittmar and Lara, 2001; Barnes et al., 2006; Lee et al., 2008; Sasaki et al., 2009). The estuary in the present study has low tidal difference (± 0.3 m) so the tidal effect on gas emission is probably not very pronounced (Botero and Salzwedel, 1999). We did not find any significant correlations between N₂O and CH₄ emissions and variables which were relatively constant among stations and seasons such as temperature, pH, redox potential and NO₂⁻ and this is probably because these variables simply did not show much variation, and therefore could not explain much of the variation in emissions of N₂O and CH₄.

In general, we did not find many differences in the water quality variables between seasons. It could be expected that there would be some differences in e.g. DO and salinity between dry and rainy season. For DO, a high rainfall could potentially give higher DO since there is a higher flow and turnover of water through the estuary but we did not observe that. Salinity would be expected to be lower in the rainy season because of an increased amount of freshwater flowing through the estuary. Nevertheless, we only found a significant difference between seasons in the sediment at Caño Dragado which was also the station that had the highest salinity overall. The station Caño Dragado is one of the areas that was seriously affected by the high salinities caused by the closure of the estuary and it seems like it is one of the places in the estuary where salinity tends to increase fastest in the dry season when the water flow through the estuary is low, probably because of a specific hydraulic pattern in the area. The reason why we did not observe significant differences in salinities between seasons is probably that it takes some months to wash out the salt meaning that there were some months with high salinity in the beginning of the rainy season. Likewise, in the beginning of the dry season there were some months with low salinity since it presumably takes a certain amount of time for the salinity to build up due to evaporation resulting in this characteristic delay in salinity. The salinities found in this study were in the range 0–43 representing values from freshwater to slightly higher than average seawater. It indicates that the rehabilitation of the area with re-establishment of the original hydrological conditions has been successful in decreasing the salinity since it used to be up to 250 in some parts of the estuary (Elster, 2000). In this study we found a significant negative correlation between salinity and N₂O emission whereas we did not find CH₄ emission to be correlated with salinity. Both N₂O and CH₄ microbial processes have been shown to be inhibited by salinity in porewater and sediment (Purvaja and Ramesh, 2001; Dalal et al., 2003). The explanation behind why CH₄ emission was not found to be correlated with salinity could be because of the large variation in our emission data on both a spatial and temporal

scale which requires a higher resolution in sampling to get more clearly established correlations. However, it could also be that because the salinity inhibition of methanogenesis can occur at low salinities as demonstrated by Baldwin et al. (2006) in a study where methane production was reduced by 30% at a salinity of only 0.7 compared to non-saline conditions. Therefore, it is possible that methanogenesis is inhibited in general at the salinities found in our study although we would still expect to find a negative correlation as found in mangroves of South India where CH₄ emission was negatively correlated with salinity which was in the range 15–34 (Krithika et al., 2008). It is also likely that the negative correlation between salinity and N₂O emission is not only because salinity inhibits N₂O production but also because the processes are stimulated by the input of water from the Magdalena River. This is freshwater with N input from discharged, untreated wastewater which brings substrate to the microbial N₂O processes and therefore adds more power to the negative correlation between salinity and N₂O emission but for another reason than the salinity effect *per se*. This pattern between N input and salinity has also been found in other studies from coastal lagoons (Herrera-Silveira, 1996; Jennerjahn et al., 2009).

We found a positive correlation between CH₄ emission and content of organic matter in the sediment showing that the microbial processes producing CH₄ are highly dependent on organic matter. The organic matter serves as substrate for the methanogenesis and content of this together with temperature and oxygen have been found to be important constraints controlling CH₄ production and oxidation from wetlands (Whalen, 2005). In the present study we also found a negative correlation between CH₄ emissions and DO which can be explained by methanogenesis mainly occurring in the anoxic one of the sediment whereas CH₄ oxidation takes place in the overlying oxic zone (Whalen, 2005; Allen et al., 2007). The positive correlation with organic matter and the negative with DO and CH₄ emission suggest that discharge of untreated wastewater which typically has high content of organic matter and low DO would result in increased CH₄ compared to an unpolluted scenario.

When the N₂O and CH₄ emissions were converted to CO₂-equivalents according to their global warming potential, there were some differences among the stations. In the dry season, Aguas Negras and Caño Grande had the highest CO₂-equivalent emissions with 340.7 and 299.7 mg m⁻² h⁻¹ whereas there were no differences in the rainy season. However, it was interesting that there were very different contributions of N₂O to the CO₂-equivalents in both seasons with Aguas Negras and Caño Dragado having the highest dominance of N₂O in the range 77.9–97.6% of the CO₂ equivalents caused by N₂O and CH₄ emissions. A study of mangroves in Australia showed that N₂O comprised 2–96% where CH₄ emission dominated during summer and N₂O during winter (Allen et al., 2007). By contrast, we did not observe differences between seasons but rather a constant high contribution of N₂O at the two stations closest to the Magdalena River. The constant high contribution of N₂O to the CO₂-equivalents is more typical for agroecosystems, where N₂O is considered to dominate CO₂-equivalent emission because of the input of N as fertilizer (Mosier et al., 2005). Again the high N₂O emission can possibly be explained by the input of wastewater from the Magdalena River, especially at Aguas Negras since this is the station closest to the river. Since N₂O has a high global warming potential of 296 and CH₄ has one of 26, it shows that discharge of untreated wastewater not only results in eutrophication of the water where it occurs but also can contribute substantially to emission of greenhouse gases. Furthermore, some mangrove areas are used for treating domestic, agricultural and industrial wastewaters in order to remove N and organic matter (Corredor and Morell, 1994; Tam and Wong, 1999).

The lack of wastewater treatment is an issue in many tropical countries although some treatment could be obtained with a cost-efficient technology as subsurface flow constructed wetlands which have been shown to be suitable for treatment of domestic wastewater in tropical Asia to protect natural wetlands (Konnerup et al., 2009; Ngo et al., 2010). It is therefore likely that this could also be an appropriate method to reduce the discharge of wastewater to the Magdalena River and other places in Colombia. Furthermore, constructed wetlands can also reduce the discharge of polluted water from tropical aquaculture systems (Konnerup et al., 2011) which also could be highly relevant in Colombia where mangroves have been used for treatment of effluent from shrimp ponds (Gauiter et al., 2001). Other studies have also shown that discharge of wastewater together with the additional N to mangrove areas can result in increased emission of especially N₂O (Kreuzwieser et al., 2003; Chen et al., 2011). This response occurs fast as demonstrated by Serena Moseman-Valtierra et al. (2011) in a study where salt marsh sediments were treated with NO₃⁻ enriched artificial seawater and the N₂O fluxes increased within 1 h compared to plots just receiving artificial seawater. Respiratory rates and CH₄ fluxes were not significantly affected by the NO₃⁻ enrichment. Liu and Greaver (2009) made a meta-analysis of 313 observations across 109 studies in order to evaluate the effect of anthropogenic N enrichment of terrestrial ecosystems on emissions of greenhouse gases. They found that across all ecosystems, N addition increased CH₄ emission by 97%, reduced CH₄ uptake by 38% and increased N₂O emission by 216%. Although there are differences between terrestrial ecosystems and wetlands, it shows how N enrichment can increase emission of both N₂O and CH₄.

In conclusion, this study showed that the mangrove sediments of Colombia's largest lagoon system are a source of N₂O and CH₄. However, there was large variability of the emissions on both temporal and spatial scale indicating that the factors controlling the emissions are complex and manifold which means that up-scaling of site observations to catchment and regional estimates should be with caution. It was found that untreated wastewater discharged into the Magdalena River and in turn, the lagoon system possibly resulted in a substantially higher emission of both N₂O and CH₄ as the wastewater contributes substrate to the processes in the form of N and organic matter. With better treatment of wastewater, it is likely that emission of both gases would be lower, especially at the sites closest to Magdalena River.

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