

Spatial and temporal variation of nitrous oxide and methane flux between subtropical mangrove sediments and the atmosphere

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Abstract

We quantified spatial and temporal variations of the fluxes of nitrous oxide (N₂O) and methane (CH₄) and associated abiotic sediment parameters across a subtropical river estuary sediment dominated by grey mangrove (*Avicennia marina*). N₂O and CH₄ fluxes from sediment were measured adjacent to the river (“fringe”) and in the mangrove forest (“forest”) at 3-h intervals throughout the day during autumn, winter and summer. N₂O fluxes from sediment ranged from an average of $-4\text{ }\mu\text{g to }65\text{ }\mu\text{g N}_2\text{O m}^{-2}\text{ h}^{-1}$ representing N₂O sink and emission. CH₄ emissions varied by several orders of magnitude from $3\text{ }\mu\text{g to }17.4\text{ mg CH}_4\text{ m}^{-2}\text{ h}^{-1}$. Fluxes of N₂O and CH₄ differed significantly between sampling seasons, as well as between fringe and forest positions. In addition, N₂O flux differed significantly between time of day of sampling. Higher bulk density and total carbon content in sediment were significant contributors towards decreasing N₂O emission; rates of N₂O emission increased with less negative sediment redox potential (E_h). Porewater profiles of nitrate plus nitrite (NO_x⁻) suggest that denitrification was the major process of nitrogen transformation in the sediment and possible contributor to N₂O production. A significant decrease in CH₄ emission was observed with increasing E_h , but higher sediment temperature was the most significant variable contributing to CH₄ emission. From April 2004 to July 2005, sediment levels of dissolved ammonium, nitrate, and total carbon content declined, most likely from decreased input of diffuse nutrient and carbon sources upstream from the study site; concomitantly average CH₄ emissions decreased significantly. On the basis of their global warming potentials, N₂O and CH₄ fluxes, expressed as CO₂-equivalent (CO₂-e) emissions, showed that CH₄ emissions dominated in summer and autumn seasons (82–98% CO₂-e emissions), whereas N₂O emissions dominated in winter (67–95% of CO₂-e emissions) when overall CO₂-e emissions were low. Our study highlights the importance of seasonal N₂O contributions, particularly when conditions driving CH₄ emissions may be less favourable. For the accurate upscaling of N₂O and CH₄ flux to annual rates, we need to assess relative contributions of individual trace gases to net CO₂-e emissions, and the influence of elevated nutrient inputs and mitigation options across a number of mangrove sites or across regional scales. This requires a careful sampling design at site-level that captures the potentially considerable temporal and spatial variation of N₂O and CH₄ emissions.

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1. Introduction

Quantification of the trace gases, nitrous oxide (N₂O) and methane (CH₄) is a subject of great interest because accurate information is required to determine the contribution of these gases to global greenhouse gas fluxes (Khalil et al., 2002; Wuebbles and Hayhoe, 2002). The

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Intergovernmental Panel for Climate Change (IPCC, 2001) has reported increased concentrations in N_2O and CH_4 since industrial times, a concern since both gases, although present in lower concentrations to that of CO_2 , have 296 (N_2O) and approximately 23 (CH_4) times the global warming potential of CO_2 over a 100-year time period (IPCC, 2001).

It is estimated that natural sources of N_2O and CH_4 account for 44–54% of N_2O emissions (9.6–10.8 Tg N_2O year⁻¹) and 30–40% of CH_4 emissions (150–237 Tg CH_4 year⁻¹) (IPCC, 2001). Tropical soils and wetlands are considered significant natural sources, contributing approximately 22–27% (N_2O) and 24% (CH_4), respectively, towards this inventory (IPCC, 2001; Whalen, 2005). Most wetland studies, however, have been carried out in temperate areas. Empirical studies in tropical wetlands are rare, and estimates of N_2O and CH_4 fluxes in tropical wetlands carry a high level of uncertainty (Purvaja and Ramesh, 2001; Purvaja et al., 2004). Tolhurst and Chapman (2005) noted that despite considerable effort, processes controlling variation in intertidal sediment properties over time remain poorly understood, as most studies have focused on only one time or spatial scale.

A major component of tropical and subtropical coastal wetlands are mangrove ecosystems, which occupy the intertidal zone of estuaries, bays, inlets and gulfs and part of the riparian zone (Alongi, 2002). Unlike temperate wetlands where temperature fluctuation is extreme, mangrove ecosystems are restricted to warm waters, with greatest abundance and species diversity found in subtropics and tropics (Alongi, 2002). Mangrove communities occur across a range of salinity levels and different types of sediments (Lovelock, 1993; Duke et al., 1998). Sediment properties of mangrove communities range from coarse sands to black fine estuary muds, and associated with sediment properties, different abiotic and biotic conditions prevail. Microbial processes affecting trace gas production are regulated by many parameters including oxygen availability, sediment temperature and water content, sediment redox potential (E_h), salinity, pH, and microbially available reduced carbon and nitrogen sources (Bauza et al., 2002; Whalen, 2005). Mangrove sediment is often considered to be oligotrophic, but mangroves are not restricted to low nutrient environments (Feller et al., 2003). There is growing interest in using mangroves for treating domestic, agricultural and industrial wastewaters (Tam and Wong, 1999). Studies have reported some capacity for mangrove estuaries to tolerate intense shrimp pond effluent (Trott and Alongi, 2000), to remove ammonium from wastewater (Tam and Wong, 1999) and to depurate nitrate from treated-sewage effluent (Corredor and Morell, 1994). The extent of such nutrient storage and conversion capacity of mangrove sediments and the potentially associated trace gas emissions remains poorly understood (Gauiter et al., 2001; Alongi, 2002).

It has been suggested that trace gas emissions from coastal mangroves are negligible compared to trace gas emissions originating from wetlands (Sotomayor et al.,

1994). However, Purvaja and Ramesh (2001) observed several human-induced factors that enhance CH_4 emissions from mangroves to the atmosphere, and there is evidence that additional nitrogen inputs in mangroves increased N_2O emissions (Kreuzwieser et al., 2003). Increasingly, riverine mangrove sediments are considered to contribute to N_2O and CH_4 emissions (Sotomayor et al., 1994; Corredor et al., 1999; Purvaja and Ramesh, 2001; Kreuzwieser et al., 2003). Another consideration is the presence of pneumatophores, the mangrove roots linking sediment to atmosphere and which have been implicated in increased emissions from mangrove sediments (Purvaja et al., 2004). The potential for mangrove sediments to have significant N_2O and CH_4 emission is of concern since mangroves occupy 181 000 km² of coastline (Alongi, 2002). As human expansion continues along riverine and coastal shorelines, mangroves may be subject to anthropogenic inputs including sewerage, aquaculture and agriculture, which have potential for adding nutrients to mangrove ecosystems (Alongi, 2002).

Some research has been undertaken to measure mangrove gas fluxes using micrometeorological techniques (Mukhopadhyay et al., 2001), however most studies have used the “closed chamber technique”, which is more readily accessible, inexpensive, easier to use, and which may capture very small variations in N_2O not measurable by flux-gradient techniques (IAEA, 1992; Griffith et al., 2002). The cost-efficient set-up of closed chambers is offset by labour intensiveness if frequent measurements are performed (Dalal et al., 2003). In agricultural systems, attention has been given to sampling strategies for temporal (Buendia et al., 1998; Smith and Dobbie, 2001) and spatial variation (Ambus and Christensen, 1994; Ball et al., 1997; Weitz et al., 1999), however, no consensus exists for measurement protocols in wetland and mangrove ecosystems.

This study was undertaken in subtropical mangrove sediments along the Brisbane River, at a site located adjacent to a treated sewage outlet, which also receives diffuse nutrient inputs from upstream (Dennison and Abal, 1999). Using the closed chamber technique we measured gas flux from exposed estuary sediments at low tide. We aimed to determine whether distinct temporal and spatial variation occurs in N_2O and CH_4 flux throughout the day and in different seasons, and whether spatial variation exists in flux. To address the second aim, we compared emissions from sediments close to the river edge (“fringe”) and in the mangrove forest (“forest”).

2. Materials and methods

2.1. Site description

Sampling was carried out approximately 46.5 km upstream from the mouth of the Brisbane River, in Chelmer, South East Queensland, Australia (27°33'S, 152°59'E), on the northern bank of a river estuarine fringe dominated by

grey mangrove (*Avicennia marina*) with river mangrove (*Aegiceras corniculatum*) understorey. Climate in this region is characterized by high humidity and rainfall during summer, with drier conditions and a wide temperature range during winter (Clark et al., 1998). Annual mean daily temperatures range between 15.5 and 25.3 °C, with mean annual rainfall 1146 mm (Bureau of Meteorology, Brisbane). The study site is approximately 0.2 ha in size and at low tide mudflats and *A. marina* pneumatophores are exposed. The site is in immediate proximity to a discharge point for Oxley Creek Sewage Treatment Plant and is part of the Brisbane River Catchment area (13 100 km²). The Brisbane River Catchment area is categorized as being under major intentional human influence, with studies over the past 50–80 years estimating a 4-fold increase in suspended sediment export from Brisbane River Catchment to Moreton Bay (to 450 000 tonnes/year), as well as increased concentrations of nitrate (22-fold to 305 µM N) and phosphate (11-fold to 42 µM P) in the water column (Dennison and Abal, 1999 and EPA, 2001 in Duke et al., 2003).

2.2. Experimental design

Sampling campaigns were undertaken during 3 seasons in April 2004 (autumn), February 2005 (summer) and July 2005 (winter). For each sampling campaign, measurements were conducted at 6.00, 9.00, 12.00, 15.00 and 18.00 h. Measurements representing different times of day were from sediments exposed during low tide, over a number of days. Each measurement campaign consisted of 10 chambers set up at two positions (5 chambers per position): “fringe” which represented the edge of the mangrove forest adjacent to the river and which was submerged at all times except at the peak of the low tide, and “forest” which was located within the mangrove forest near the shore line and which was submerged only at high tide. Since the distance between the fringe and the forest position was within 20 m, the sampling may have included the “transition” zone in the fringe measurements. During each campaign gas samples were collected and environmental variables measured, with sediments sampled for subsequent analyses. The number of pneumatophores per chamber was also counted during each gas sampling campaign.

2.3. Measurements of sediment gas fluxes

The closed chamber method was used to quantify fluxes across the sediment–atmosphere interface. Measurements were taken using PVC pipe (diameter 23.5 cm, length 25 cm, volume 10.84 L, enclosing 0.043 m²) and Perspex Chambers (length 20 cm, volume 8 L, enclosing 400 cm²), with initial trials showing no significant differences in measurements between chamber design. Chamber lids were fitted with a Teflon septum port and vent tube through which gas samples were taken using a gas-tight syringe (Hamilton, Australia). Chambers were inserted 3 cm into

sediments for each series of measurements, which is adequate to ensure minimal lateral gas leakage, in fine textured, wet sediment (Hutchinson and Livingston, 2001). Some variation in insertion depth occurred in softer sediment, however this was carefully recorded to ensure sampling volume of chamber was correctly estimated. Chambers were left open for approximately 15–30 min prior to sampling, which is sufficient time to preclude immediate impacts of any root disturbance caused by the chamber insertion (Keller et al., 2000). Deployment time was set at 1 h, with sampling at 0, 30 and 60 min intervals. Fluxes were calculated using linear least-square fit of the time series of gas concentrations. Increases of N₂O and CH₄ fluxes over the incubation period were linear ($R^2 > 0.95$).

Gas samples were taken using a 10 mL gas-tight syringe (Hamilton, Australia), and transferred into 12 mL pre-evacuated Exetainers for storage (Labco Limited, USA), which have been found adequate at maintaining integrity of gas samples (Laughlin and Stevens, 2003). All samples were stored cool and transported to the laboratory, where they were analysed within 24 h using gas chromatography (Auto-system, Perkin-Elmer (PE), USA; 3800, Varian, Netherlands). Instrument specifications are listed for the Perkin Elmer and the Varian GC, respectively: gas samples were loaded into two sample loops (2.5 mL & 3 mL length) and injected (150 °C) onto two columns (Hayesep-Q; Porapak). N₂ was used as a carrier gas for PE; Varian used N₂ (N₂O) and He (CH₄) carrier gases for detection at flow rates of 20 and 25 mL min⁻¹, respectively. N₂O was measured using a ⁶³Ni electron capture detector (temperature 300 °C) with CH₄/Ar as auxiliary gas (20 mL min⁻¹). CH₄ was detected by FID (temperature 200 °C) with flow rates of air (800 mL min⁻¹) and H₂ (90 mL min⁻¹), as per (Kreuzwieser et al., 2003). All gases and standards were certified by BOC gases (Brisbane, Australia). Standards (0.5 ppm N₂O and 2 ppm CH₄ in N₂) appeared after 2.1 and 1.4 min, respectively. Gas concentrations were quantified by comparing peak areas of samples against standards run every 8–10 samples, ensuring each sample run maintained RSD below 6%.

2.4. Measurement of environmental factors

For each chamber measurement, sediment cores (5 cm long; 3 cm wide) were measured for gravimetric water content, bulk density, water filled pore space (%WFPS), volumetric water content, and total C, N and S concentration. The concentration of dissolved inorganic nitrogen (NH₄⁺-N, NO₃⁻-N) of each replicate was measured at 06.00, 12.00 and 18.00 h. Sediment E_h and sediment surface temperature were measured at 5-min intervals in each position (forest and fringe) for the duration of chamber closure, during each series of gas measurements.

Sediment characteristics were determined as per Linn and Doran (1984) as follows:

Gravimetric water content of sediment (θ_m , $\text{gH}_2\text{O g}^{-1}$ dry sediment) = (weight of wet sediment—weight of dry sediment at 105°C)/weight of dry sediment at 105°C . Bulk density (BD, g cm^{-3}) = weight of dry sediment sample at 105°C /total volume of sediment sample. Volumetric water content (θ_v , $\text{gH}_2\text{O cm}^{-3}$ sediment) = (θ_m) (BD). Total Porosity (TP) was estimated as $1 - (\text{bulk density/particle density})$, where particle density was taken as 2.65 g cm^{-3} . Water filled pore space (%WFPS) was calculated as (θ_v/TP) (100).

Subsamples from sediment cores were used for dissolved NH_4^+ -N and NO_3^- -N analysis. Five g sediment slurry was diluted with 2 M KCl (1:10); NO_3^- -N was determined according to Rayment and Higginson (1992) and NH_4^+ -N according to Baethgen and Alley (1989). A subset of sediment samples was dried at 40°C in a drought oven, ground to $<1 \text{ mm}$ size and analysed for total C, N and S using an element analyzer LECO CNS 2000 (Rayment and Higginson, 1992). NH_4^+ -N and NO_3^- -N, and total C, N and S concentrations in the sediment were expressed on oven-dry (105°C) weight basis. Redox potential (E_h) was recorded at 5-min intervals using a platinum electrode and a silver/silver chloride reference electrode (ORP300; Greenspan technology Pty Ltd, Australia). E_h measurements were made at 5 cm depth of the sediment using a core.

2.5. Porewater profiles

Three replicate sediment cores were sampled each from fringe and forest positions during February sampling campaign and incubated in 10 L of in situ water overnight at room temperature (24°C) before analysis of O_2 and NO_3^- plus NO_2^- (NO_x^-) profiles using microsensors. The oxygen sensor was constructed as described in Revsbech (1989), and a microbiosensor for NO_x^- (NO_3^- plus NO_2^-) was constructed as described in Larsen et al. (1997). N_2O profiles were also measured using a N_2O microsensor (Andersen et al., 2001), but the N_2O levels were below the $1 \mu\text{mol L}^{-1}$ detection limit of the sensor. Profile measurements and data acquisition was performed as per Meyer et al. (2005), and NO_x^- production and consumption rates were calculated from the concentration profiles using the diffusion reaction model by Berg et al. (1998). In short, the production and consumption of chemical species can be calculated from the second derivative of their steady-state concentration profiles, meaning that a convex curvature indicates production, and a concave curvature indicates consumption. These calculations are based on Fick's second law of diffusion (Crank, 1983; Revsbech and Jorgensen, 1983) and the effective diffusion coefficient of the species in the particular substrate. The diffusion coefficient NO_x^- in the sediment (0.0000185) was calculated as the diffusion coefficient of NO_3^- in water at 24°C (Li and Gregory, 1974) times the sediment porosity (Ullman and Aller, 1982). Sediment porosity (0.94 in the fringe and 0.82 in the forest) was determined by measuring the wet

weight and dry weight (after 24 h of drying at 105°C) of the upper 5 mm of the sediment cores.

2.6. Conversion to CO_2 -equivalents

Global warming potentials of 296 for N_2O and 23 for CH_4 (IPCC, 2001) were used to convert N_2O and CH_4 emissions to $\text{CO}_2\text{-e}$ for comparing their greenhouse impacts.

2.7. Statistical analysis

All statistical analyses were carried out using Statistica Software (Carver, Brooks/Cole, Canada). Statistical significance of differences at $P < 0.05$ between means were calculated using GLM-ANOVA (ln- CH_4) and Kruskal–Wallis ANOVA (N_2O). Correlations between log-transformed emissions and independent variables were calculated using step-wise multiple regression analysis (case-wise elimination). Results at $P < 0.05$ level of significance are indicated by different letters following mean values in the tables and figures.

3. Results

3.1. N_2O and CH_4 fluxes from mangrove sediment

Over all sampling periods, N_2O fluxes ranged from -4 to $65 \mu\text{g N}_2\text{O m}^{-2} \text{ h}^{-1}$ and differed significantly between seasons ($P < 0.01$, Fig. 1). With the exception of July 06:00 sampling, sediments were found to be a net source of N_2O emissions during all times of day and the seasons measured. Significantly higher N_2O emission was observed in the fringe compared to forest position during February 12:00 sampling, and for July 06:00, 09:00 and 12:00 ($P < 0.05$; Fig. 1). In contrast, April 09:00 sampling recorded significantly higher emissions in the forest compared to fringe position. N_2O flux varied significantly during different times of the day at fringe and forest positions during April sampling; also at fringe position during July sampling ($P < 0.05$; Fig. 1).

Methane emission rates averaged between $3 \mu\text{g CH}_4 \text{ m}^{-2} \text{ h}^{-1}$ and $17.37 \text{ mg CH}_4 \text{ m}^{-2} \text{ h}^{-1}$ and varied significantly between seasons ($P < 0.01$; Fig. 2). CH_4 emission was significantly higher at the fringe compared to forest position in autumn (April) and summer (February) but not winter (July) ($P < 0.01$; Fig. 2). Time of day of sampling had no effect on CH_4 emission at fringe or forest positions during any of the seasons sampled (Fig. 2).

Across all three seasons sampled, the site was a net source of N_2O and CH_4 . CH_4 emissions decreased significantly between April 2004 to July 2005 ($n \log \text{CH}_4 = 10.9 - 2.5x$; $R = -0.81$, $P < 0.001$), but not for N_2O (Table 1). When N_2O and CH_4 emissions were expressed as $\text{CO}_2\text{-e}$ emissions, N_2O emissions contributed between 1.7% and 18% of net $\text{CO}_2\text{-e}$ emissions measured during April and February, although contribution of N_2O

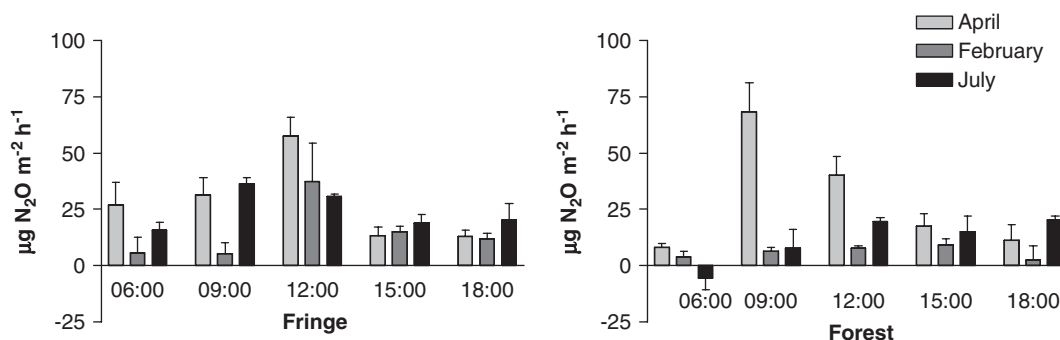


Fig. 1. N_2O flux ($\mu\text{g N}_2\text{O m}^{-2} \text{h}^{-1}$) measured at three hourly intervals in autumn (April 2004), summer (February 2005) and winter (July 2005) in mangrove sediment, Brisbane River, Australia. Data represent averages and standard errors (SE) of 5 sampling points at fringe and forest positions.

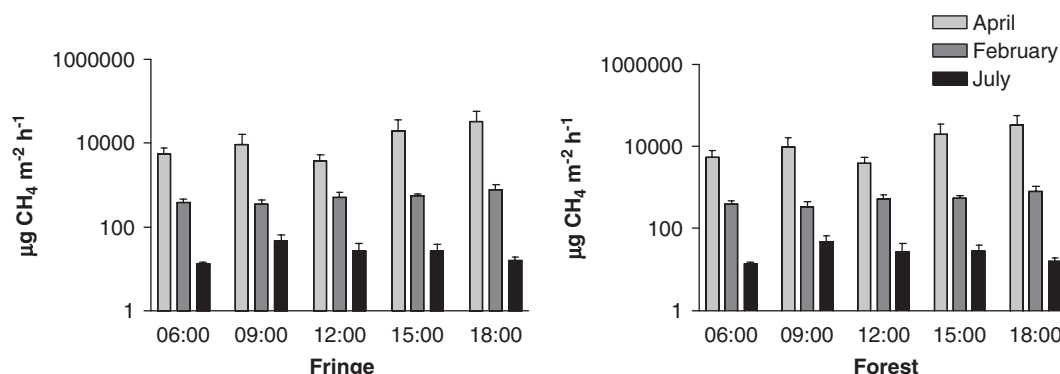


Fig. 2. Methane flux ($\mu\text{g CH}_4 \text{m}^{-2} \text{h}^{-1}$) at fringe and forest positions in autumn (April 2004), summer (February 2005) and winter (July 2005) in mangrove sediment, Brisbane River, Australia. Bars represent averages and standard error (SE) of 5 sampling points at fringe and forest positions.^a

Table 1
Estimated total N_2O and CH_4 emission ($\mu\text{g CO}_2$ equivalents $\text{m}^{-2} \text{h}^{-1}$) during the 2004/5 sampling period in mangrove sediment, Brisbane, Australia

	April 2004		February 2005		July 2005	
	N_2O	CH_4	N_2O	CH_4	N_2O	CH_4
Fringe	8435 ± 2688	107658 ± 66879	4498 ± 2601	80509 ± 49073	7243 ± 1552	1591 ± 1598
Forest	8636 ± 3440	340451 ± 287522	1779 ± 900	11988 ± 3215	3320 ± 1877	601 ± 255
Combined	8536 ± 2104	221700 ± 143361	3138 ± 1382	46248 ± 25656	5240 ± 1312	1086 ± 775
Fringe & Forest	(1.7–12%)		(2.3–18%)		(67.8–95.6%)	

Estimates were derived by weighted averages of 50 data points from morning to late afternoon (6.00, 09.00, 12.00, 15.00, 18.00 h) for each sampling month. The IPCC (2001) conversion of N_2O and CH_4 emissions to CO_2 equivalents is 296 and 23, respectively, over a 100-year timeframe. Percentage contribution (reported as a range) of N_2O during each season is given in parentheses.

to net $\text{CO}_2\text{-e}$ emissions was higher in July (winter) sampling, comprising 67–95% of net $\text{CO}_2\text{-e}$ measured (Table 1).

3.2. Sediment variables

$\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, total N and total C in the mangrove sediment decreased significantly over the sampling period (Table 2). Significant decreases in total N and total C were observed during July compared to April and February seasons; $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ differed significantly between seasons ($P < 0.01$; Table 2). No significant difference

in total S content was observed during seasons sampled. Sediment temperatures ranged between 16°C in winter and 26°C in summer; sediment temperature did not differ between times of day for any of the seasons sampled, although significant differences between fringe and forest positions for each season were identified (Table 2). E_h was negative and ranged between -131 mV (April 2004) and -39.6 mV (July 2005), with no significant differences observed between fringe and forest positions recorded during any of the sampling campaigns (Table 2).

Relationships between $\ln \text{N}_2\text{O}$ and $\ln \text{CH}_4$ fluxes and independent variables bulk density, % water filled pore

Table 2
Sediment parameters over the 2004/5 sampling campaign

Sediment variables	Sampling date		
	Apr-04	Feb-05	Jul-05
Total C (mg/kg)	24775 ± 713 ^A	24125 ± 532 ^A	20262 ± 628 ^B
Total N (mg/kg)	1868 ± 35 ^A	1819 ± 69 ^A	1440 ± 65 ^B
NH ₄ ⁺ -N (µg g ⁻¹)	580 ± 30 ^A	100 ± 10 ^B	50 ± 10 ^C
NO ₃ ⁻ -N (µg g ⁻¹)	25 ± 8 ^A	1 ± 0.07 ^B	8 ± 2 ^C
Temperature (°C)			
Fringe	24.6 ± 0.6 ^A	27.5 ± 0.5 ^B	17.3 ± 0.4 ^C
Forest	26.0 ± 0.9 ^A	25.8 ± 0.2 ^A	16.3 ± 0.2 ^B
Eh (mV)			
Fringe	-117.5 ± 19.9	-86.7 ± 12.8	-40.6 ± 14.9
Forest	-131.3 ± 16.2	-80.3 ± 14.3	-39.6 ± 18.1
Bulk Density			
Fringe	0.66 ± 0.03	0.70 ± 0.02	0.55 ± 0.03
Forest	0.73 ± 0.04	0.84 ± 0.03	0.60 ± 0.05
% WFPS			
Fringe	71.7 ± 2.6	72.5 ± 2.7	84.8 ± 4.9
Forest	78.9 ± 2.9	56.8 ± 4.1	70.4 ± 5.4

Data are weighted means of six samples collected from fringe and forest positions at 06.00, 12.00 and 18.00 h for each sampling date (±SE). Statistically significant differences between sampling dates ($P < 0.05$) were calculated for multiple comparisons using Kruskal–Wallis ANOVA and are indicated by different letters within each row.

Table 3
Regression analysis of lnN₂O and CH₄ emissions at and sediment physical and chemical parameters^a

Sediment parameter	R value	
	lnN ₂ O	lnCH ₄
Bulk density	-0.38*	0.42 *
% water filled pore space (%WFPS)	0.21 *	-0.07 n.s.
Eh	0.13 *	-0.64 *
Sediment temperature	-0.21 n.s.	0.76 *
Total N	-0.27 n.s.	0.46 *
Total C	-0.46 *	0.41 *
Total S	-0.03 n.s.	0.05 n.s.
NH ₄ ⁺ -N	0.27 *	0.24 *
NO ₃ ⁻ -N	0.31 *	0.50 *

Significant R values are highlighted at the $P < 0.05$ (*) level of significance.

^aCorrelations of NH₄⁺-N and NO₃⁻-N and trace gases was undertaken from a subset of samples taken at 06.00, 12.00 and 18.00 h.

space (WFPS), E_h , and sediment temperature, NH₄⁺-N, NO₃⁻-N and total C, N and S are given in Table 3. A subset of these variables, which focused upon data collected only during 06.00, 12.00 and 18.00 h, was used for stepwise multiple regression analysis to include the independent variables that significantly ($P < 0.05$) accounted for the variation in N₂O and CH₄ emissions. Of the variables compared using multiple regression analysis, total C and E_h significantly contributed towards decreased lnN₂O emission ($R^2 = 0.63$, $P < 0.05$) whilst for lnCH₄ sediment temperature and to a lesser extent, NH₄⁺-N, significantly

contributed towards CH₄ emission ($R^2 = 0.76$, $P < 0.05$). Pneumatophore numbers per chamber were generally very low (< 5 per chamber); no relationship between pneumatophore number per chamber and N₂O or CH₄ emissions was found.

Microsensor measurements showed similar O₂ porewater profiles in the fringe and forest samples, but deeper penetration of NO_x⁻ in the forest position (Fig. 3) reflecting a lower rate of NO_x⁻ reduction rate in the forest sediment. The integrated NO_x⁻ production and consumption rates per cm² sediment surface, corresponding to the size of the hatched areas of Fig. 3, were 50 and 134 µmol cm⁻² s⁻¹ in the fringe position, and 24 and 71 µmol cm⁻² s⁻¹ in the forest position. Hence the rate of NO_x⁻ production (nitrification) corresponded to less than half of the NO_x⁻ reduction, leading to a net uptake of NO_x⁻ from the water phase as seen from the slope of the concentration profile in Fig. 3. It should be noted that NO_x⁻ reduction represents the sum of denitrification, dissimilative reduction of NO₃⁻ to NH₄⁺, NO_x⁻ assimilation, and anammox (the anaerobic oxidation of NH₄⁺ to NO₂⁻). Of these processes, only denitrification is known to accumulate N₂O.

4. Discussion

Our results demonstrate that mangrove sediments in the subtropical estuary provide a net source of N₂O and CH₄. When N₂O and CH₄ emissions were converted to CO₂-e emissions using their global warming potentials, CH₄ comprised between 94% and 98% of total calculated CO₂-e emissions, with largest emissions occurring during summer (February) and autumn (April) seasons (Table 1). Although this contrasts the notion proposed for agroecosystems, where N₂O is considered to dominate CO₂-e emissions (Mosier et al., 2005), N₂O dominated winter CO₂-e emissions at both fringe and forest positions (67–95%) when CH₄ emissions were lowest (Table 1). This finding highlights the importance of adequately capturing seasonal variation of both N₂O and CH₄ in subtropical mangrove sediments, particularly during times of low CH₄ emission, where the high global warming potential of N₂O can dominate trace gas emissions.

Seasonal variation in CH₄ emissions from mangroves sediments was observed in this study (Fig. 2) and also reported by others (Sotomayor et al., 1994; Mukhopadhyay et al., 2001; Purvaja et al., 2004). Whalen (2005) observed that annual patterns of CH₄ emission are influenced by latitude, with arctic, boreal and some temperate regions characterized by pronounced CH₄ emissions, which are governed by seasonal variability in temperatures affecting water availability, production of substrate precursors and microbial activity (Q_{10}). In contrast, temperature variation in tropical and subtropical wetlands is less extreme, and CH₄ emissions are linked to annual high and low water cycles (Whalen, 2005). Daily and annual water cycles, such as summer 'wet' season, play

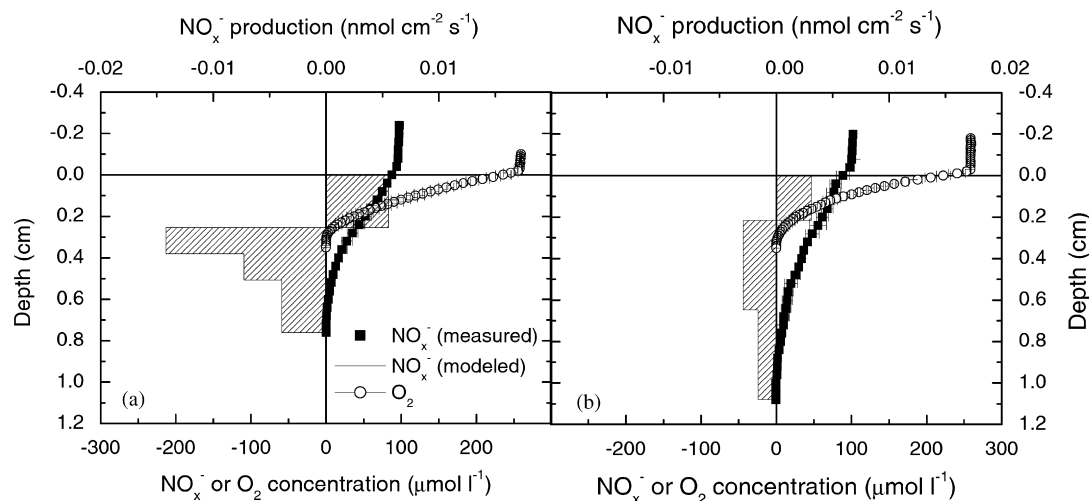


Fig. 3. Porewater profiles of NO_x^- (■) and O_2 (○) and calculated NO_x^- production rates (hashed areas) in sediment from the river fringe (a) and mangrove forest (b) during the February sampling period. Negative NO_x^- production indicates consumption.

important roles in regulating sediment nutrient status (Tam and Wong, 1998). Eyre et al. (1998) found that episodic, short-lived, large freshwater inputs during summer, impacts significantly on sub-tropical catchment hydrology, salinity and biology. This is of particular interest in estuarine mangroves, since some estuaries experience longer residency time of nutrients and tidal flushing compared to coastal regions (Dennison and Abal, 1999) and salinity in porewaters and sediments, known to inhibit N_2O and CH_4 microbial processes (Denier van der Gon and Neue, 1995; Purvaja and Ramesh, 2001; Dalal et al., 2003) can be further diluted via upstream and groundwater inputs.

Purvaja and Ramesh (2001) proposed that rising soil temperatures and degradation of soil organic matter contributed to strong summer and pre-monsoon peaks in CH_4 emission in mangrove sediments, whilst monsoonal floodwaters possibly restricted CH_4 emissions. We observed a significant positive relationship between sediment temperature and CH_4 emission, and this was likely due to a combined effect of reduced organic matter and lower winter temperatures that resulted in decreasing CH_4 emission during the April 2004–July 2005 study period (Table 2). Comparatively little attention has been given to seasonal variation in N_2O flux in wetlands, including mangrove ecosystems. N_2O flux in mangrove ecosystems has been measured in one or two seasons only, or N_2O flux was pooled across seasons, making comparisons of our results with the literature difficult. Significant seasonal variation in N_2O emissions however, has been noted in temperate wetlands (Liikanen et al., 2006) and in this study (Fig. 1), where N_2O emissions dominated $\text{CO}_2\text{-e}$ emissions in the winter sampling.

In addition to seasonal changes in sediment parameters and associated trace gas fluxes, temperature and water fluctuations occur at tidal and diurnal time-scales and influence structure, chemical properties and biological

activity of sediments. Tidal pattern and daily rainfall events affect salinity, oxygen and redox potentials in sediments and porewaters, combining with fluctuations in daily temperature to influence turnover of microbially-available nutrients and faunal activity, driven by water column and sediment exchange (Tolhurst and Chapman, 2005). Although not measured in this study, variations in water table position have been reported to influence CH_4 emissions (Whalen, 2005) and it is likely that they provide an important source of fresh water input to some estuary mangrove sediments.

We found emissions varied significantly throughout different times of the day for N_2O (Fig. 1) but not for CH_4 (Fig. 2). Diurnal variation in trace gas flux has been reported in other mangrove ecosystem studies, with emissions peaks for N_2O coinciding with increased ammonium production at night and for CH_4 , the times of tidal inundation (Bauza et al., 2002; Yi Lu et al., 1999). Other tropical flooded wetlands had high seasonal variability of CH_4 emissions but did not report significant diurnal variation (Devol et al., 1990; Wassmann et al., 1992). It was beyond the scope of our study to measure N_2O and CH_4 fluxes over the complete tidal inundation cycle although this would reveal the extent of diurnal variation of N_2O flux and whether CH_4 flux from sub-tropical mangroves undergoes strong diurnal cycles.

Environmental drivers influencing emissions at temporal scales may also influence physical and chemical parameters of sediment at spatial scales, where site-specific conditions such as topography, aspect, slope and species composition may determine impact of seasonal and daily temperature and water cycles. We recorded significantly higher N_2O emissions from sediment at mangrove fringe compared to forest positions only at two occasions (July 09:00 and February 12:00; Fig. 1), whilst CH_4 emission was significantly higher in sediment at river fringe compared to forest across all times of day sampled in summer

(February) and winter (July) (Fig. 2). Although no significant spatial differences in nutrient level was observed (Table 2), nearly all of the N_2O observations recorded slightly higher temperatures in fringe compared to forest positions; microsensor analysis of February mangrove sediments also showed higher activity of N transforming activity in fringe compared to forest positions (Fig. 3). It is possible that local radiative and hence temperature differences due to aspect, slope and canopy shading influenced spatial differences between-replicates and at spatial levels. In other mangrove ecosystems, greatest emissions of CH_4 have been reported from the ‘transition zone’ between fringe and forest positions (Sotomayor et al., 1994), whilst N_2O emission decreased from seaside to forest zone (Bauza et al., 2002), or were higher in transition zone between *Avicennia* and *Rhizophora* mangroves (Corredor et al., 1999). In our study, river fringe and mangrove forest were in close proximity (<20 m), dominated by one mangrove species, and emissions from the transition zone would have likely been captured within the river fringe measurements.

Mangrove species and root-structure may also effect sediment trace gas production. The presence of mangrove conduit-roots, so-called pneumatophores, can influence transportation of trace gases to the sediment surface. Pneumatophore numbers were generally very low (<5 per chamber) and no relationship between pneumatophore number and emissions was observed in our study, although others report mixed responses ranging from no relationship, to strong correlation between pneumatophore number per unit area and trace gas emissions (Kreuzwieser et al., 2003; Purvaja et al., 2004). Although their role remains unclear, further inclusion of pneumatophores in experimental design of trace gas measurement in mangrove sediments is important, as it is possible that this relationship is site-specific, dependent on pneumatophore size, density and seasonal growth rates of pneumatophores.

There is still limited understanding of the key abiotic variables, their interactions at temporal and spatial scales and their effects on N_2O and CH_4 emissions, yet, such understanding is essential for devising management strategies to minimize trace gas emissions. In mangrove ecosystems, site-level control of N_2O production has been attributed to nitrification, when sediment has high ammonium levels and positive E_h (Corredor et al., 1999; Bauza et al., 2002; Munoz-Hincapie et al., 2002) or to denitrification, when sediment has high nitrate levels and sediment E_h is negative (Kreuzwieser et al., 2003). We measured negative sediment E_h and a significant relationship between sediment nitrate levels and N_2O emission; further, microsensor measurements revealed 2- to 3-fold higher NO_x^- reduction rates compared to nitrification rates (Fig. 3), which suggests that denitrification was the main process controlling N_2O flux. N_2O emission decreased with greater total C content and bulk density in sediments (Table 3), with a positive relationship between total C and bulk density in sediments observed ($r = 0.35$, $P < 0.05$).

Although we detected a weak but significant positive relationship between total C and nitrate concentrations in sediment ($r = 0.28$; $P < 0.05$), no significant relationship occurred between N_2O flux and C/nitrate ratio in sediments; a possible explanation may be that sediments with higher total C and bulk densities decreased diffusivity of gas, causing N_2O molecules to be reduced to N_2 (Smith et al., 2003).

Purvaja et al. (2004) observed that microbial processes form the next level of analysis required to understand controls of methane emission from mangroves. Oxygen, temperature and substrate supply have been identified as important constraints controlling CH_4 production and oxidation from wetlands (Whalen, 2005). In addition to these controls, water level, E_h , salinity, and sulphate concentrations are considered dominant processes controlling methane emissions from mangrove communities (Yi Lu et al., 1999; Purvaja and Ramesh, 2001; Kreuzwieser et al., 2003; Purvaja et al., 2004); our results also found CH_4 emissions to increase significantly with reducing E_h , sediment temperature, and amounts of total N and C, NH_4^+ -N and NO_3^- -N in sediments (Table 3). Whalen (2005) also observed that individual process-level controls on CH_4 production/oxidation frequently show nonlinear interactions in wetlands, which are characteristically dynamic spatiotemporally with respect to environmental drivers, from hours to years and at spatial scales of <1 m. Similarly, the temporal distribution of N_2O flux tends to be log-normally skewed in most ecosystems (Dalal et al., 2003). Consideration should therefore be given to initial sampling efforts at site-level, to minimise pseudo-replication and masking of spatio-temporal effects, by recording (where possible) sediment parameters at individual chamber-levels rather than pooled data representing spatial or temporal values.

In our study, N_2O emissions were mostly higher (5.4 ± 4.7 to $68 \pm 12.9 \mu\text{g N}_2\text{O m}^{-2} \text{h}^{-1}$; Fig. 1) than in other mangrove sediments with assumed treated sewage inputs, (Puerto Rico, $4.4 \mu\text{g N}_2\text{O m}^{-2} \text{h}^{-1}$; Brisbane River $13 \pm 11 \mu\text{g N}_2\text{O m}^{-2} \text{h}^{-1}$) (Corredor et al., 1999; Kreuzwieser et al., 2003). CH_4 emissions during winter, averaging 26 ± 5 to $66 \pm 30 \mu\text{g CH}_4 \text{m}^{-2} \text{h}^{-1}$ (Fig. 2), matched emissions recorded at a nearby mangrove forest with assumed nutrient input from treated sewage (Kreuzwieser et al., 2003). Summer CH_4 emissions were over 50 times greater than reported previously by Kreuzwieser et al. (2003) with maximum CH_4 emissions obtained during our study ($19 \text{ mg CH}_4 \text{m}^{-2} \text{h}^{-1}$; Fig. 2) similar to the lower end of CH_4 emissions recorded in Indian estuary sediments subjected to sewage input (Purvaja and Ramesh, 2001). However, comparison of N_2O and CH_4 emissions from our study to other mangrove sites of similar conditions is difficult because it appears that the current classification of mangroves into ‘impacted’ and ‘unimpacted’ categories is arbitrary, with determinations of impact levels based upon different measured nutrients in sediments or porewaters. Subsequently, CH_4 emissions from mangroves that were

classified as ‘unimpacted’ range from comparatively low ($140 \mu\text{g CH}_4 \text{m}^{-2} \text{h}^{-1}$) to very high ($13 \text{mg CH}_4 \text{m}^{-2} \text{h}^{-1}$) (Yi Lu et al., 1999; Kreuzwieser et al., 2003, Purvaja and Ramesh, 2001).

More helpful for local, regional, and global comparisons of mangrove sediments would be to assign agreed human impact status to sites, e.g. similar to Purvaja and Ramesh (2001), where sites are quantified according to seasonal variation in soil nutrient and porewater status; received run-off via direct and indirect inputs; sources of fresh water inputs, and frequency of rainfall and tidal flushing (which influences nutrient residency time). Further to this, determination of an agreed sampling methodology would enable monitoring of changes occurring from human activities, such as changes in nutrient inputs, or to hydrological conditions via human activity eg. redirection of fresh water inputs or tidal flows.

Upscale of emissions from mangroves sediments to annual inventories has been undertaken for CH_4 only, but no agreed methodology exists (Sotomayor et al., 1994; Mukhopadhyay et al., 2001; Purvaja and Ramesh, 2001). Our study highlights the need (i) to adopt a least-intensive sampling protocol at site-level, which identifies magnitude of N_2O and CH_4 variation at seasonal, diurnal and spatial scales, before values are up-scaled to annual inventories (ii) to devise an improved classification system for determination of level of impact on mangroves, based upon the quantification of nutrient inputs in sediments, tidal and ground waters, tidal flushing and amount of fresh water influence and (iii) to further identify key drivers of trace gas emissions in mangrove estuaries to understand the causalities of spatial and temporal variations, in order to initiate the changes required for reducing trace gas emissions. In conclusion, although CH_4 accounted for most of the calculated $\text{CO}_2\text{-e}$ emissions from our study, the distinct seasonal variation of both trace gas emissions, combined with the high global warming potential of N_2O , demonstrated that N_2O contributions can be of importance during winter when CH_4 emissions may be lower than in summer months.

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