

# Tidal dynamics and rainfall control N<sub>2</sub>O and CH<sub>4</sub> emissions from a pristine mangrove creek

J. Barnes, R. Ramesh, R. Purvaja, A. Nirmal Rajkumar, B. Senthil Kumar, K. Krithika, K. Ravichandran, G. Uher, and R. Upstill-Goddard

Received 8 May 2006; revised 9 June 2006; accepted 5 July 2006; published 12 August 2006.

[1] Dissolved CH<sub>4</sub>, N<sub>2</sub>O, O<sub>2</sub>, and inorganic nitrogen nutrients (NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup>) were measured over tidal cycles in pristine Wright Myo mangrove creek waters during dry and wet seasons. Dissolved CH<sub>4</sub> and N<sub>2</sub>O showed no seasonality (dry season; 491  $\pm$  133 nmol CH<sub>4</sub> 1<sup>-1</sup>, 9.0  $\pm$ 2.3 nmol N<sub>2</sub>O l<sup>-1</sup>, wet season;  $466 \pm 94$  nmol CH<sub>4</sub> l<sup>-1</sup>,  $8.6 \pm 1.3$  nmol N<sub>2</sub>O l<sup>-1</sup>). Creek water dissolved gas and inorganic nitrogen distributions reflect sediment porewater release during hydrostatic pressure drop toward low water. Creek water CH<sub>4</sub> emission was suppressed by oxidation during rainfall, consistent with changes to dissolved nitrogen speciation, although N2O emissions were unaffected. Scaling up emissions flux estimates from mangrove creek waters and intertidal sediment gives worldwide mangrove emissions  $\sim 1.3 \times 10^{11}$  mol CH<sub>4</sub> yr<sup>-1</sup> and  $2.7 \times 10^9$  mol N<sub>2</sub>O yr<sup>-1</sup>; mangrove ecosystems are thus small contributors to coastal N2O emissions but could dominate coastal CH4 emissions. Comparing our data with mangrove CO<sub>2</sub> fluxes, mangrove ecosystems could be small net contributors of atmospheric greenhouse gases. Citation: Barnes, J., R. Ramesh, R. Purvaja, A. Nirmal Rajkumar, B. Senthil Kumar, K. Krithika, K. Ravichandran, G. Uher, and R. Upstill-Goddard (2006), Tidal dynamics and rainfall control  $N_2O$  and  $CH_4$  emissions from a pristine mangrove creek, Geophys. Res. Lett., 33, L15405, doi:10.1029/2006GL026829.

## 1. Introduction

[2] Mangroves cover ~75% of tropical coastlines and are among the world's most productive ecosystems. About one half of mangrove net primary production is exported to coastal shelves [Dittmar et al., 2006]; the remainder is buried and/or recycled, some being exported to the atmosphere from heterotrophic mangrove waters and sediment, as CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub>. Measurements of these emissions are relatively few and no simultaneous studies of fluxes from both mangrove forest sediment and surrounding creek waters exist. We discuss CH<sub>4</sub>, N<sub>2</sub>O, O<sub>2</sub> and inorganic nitrogen dynamics, and CH<sub>4</sub> and N<sub>2</sub>O emissions fluxes from pristine mangrove forest sediment and creek waters estimated during dry and wet season tidal cycles. Combining these with available emissions fluxes of CO<sub>2</sub>, we

Copyright 2006 by the American Geophysical Union.

0094-8276/06/2006GL026829\$05.00

discuss the potential contribution of mangrove ecosystems to the greenhouse gas budget of the atmosphere.

#### 2. Sites and Methods

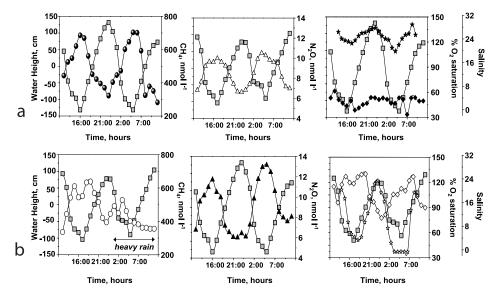
- [3] Wright Myo (11°47′27.7″N, 92°42′24.3″E) is a small, tropical tidal mangrove creek (~8 km long, 20–40 m wide dependant on tidal state) on South Andaman Island, 1200 km east of mainland India. The Andaman Island mangroves are sparsely populated and among the worlds most pristine. Vegetation is dominated by dense *Rhizophora* sp. stands naturally shielded from strong winds and waves; the surrounding area is mainly hilly, forest vegetation.
- [4] We sampled over full tidal cycles: 12:30–11:30 hrs, 23–24 January 2004 (dry season); 13:00–12:00 hrs, 21–22 July 2004 (wet season). Mean tidal ranges and water depths respectively were: January, 0.07–2.21 m and 3.2 m; July 0.69–2.77 m and 3.4 m. For both surveys high tide was around midnight, with low tides around sunset and sunrise.
- [5] Water samples (0.5 m) for CH<sub>4</sub> and N<sub>2</sub>O analyses were collected hourly from mid creek, inoculated with HgCl<sub>2</sub>, dark stored at 4°C for <6 hours, and analyzed by gas chromatography with a precision (1 $\sigma$ ) of ±1% [*Upstill-Goddard et al.*, 1996]. Filtered samples (Whatman 0.4  $\mu$ m) for NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> were stored frozen at -20°C and analyzed by standard colorimetry; analytical precisions (1 $\sigma$ ) were better than ±2%. Salinity, temperature, turbidity and dissolved O<sub>2</sub> were measured on site with a portable probe (Horiba U-10); precisions (1 $\sigma$ ) were ±0.01 salinity, ±3% turbidity, ±0.3°C, and ±0.01 mg O<sub>2</sub> l<sup>-1</sup>. Wind speed was recorded as one minute means with a hand held cup anemometer (Lutron LM8000: resolution ±0.1 m s<sup>-1</sup>).
- [6] Emissions fluxes of CH<sub>4</sub> and N<sub>2</sub>O were measured directly from mangrove forest sediment (0.2 m<sup>3</sup> static chamber, both seasons) and surrounding creek waters (0.02 m3 free-floating chamber, wet season) [Purvaja and Ramesh, 2001; Purvaja et al., 2004]. For the static chamber a base collar inserted 10 cm into the sediment about 3 hours prior to sampling minimized lateral creek water inflow. Sampling commenced at sunrise low tide. Chamber sediment was water covered throughout both deployments; water depths increased from ~8 to ~15 cm during sampling. Chamber air was mixed with a D.C. pump and sampled every 20 minutes until the base collar detached from the sediment in the rising tide, giving  $\sim$ 3 hours of data. The free floating chamber was deployed in mid creek just after midnight high tide on 22 July 2004. Headspace was sampled every 30 min. for 3 hours. Deployment coincided with four hours of torrential rain from 0100 hours; about 6-8 cm of rain fell during this period. Creek water fluxes (both surveys) were also estimated using F =

**L15405** 1 of 6

<sup>&</sup>lt;sup>1</sup>Ocean Research Group, School of Marine Science and Technology, University of Newcastle upon Tyne, Newcastle Upon Tyne, UK.

<sup>&</sup>lt;sup>2</sup>Institute for Ocean Management, Anna University, Chennai, India.

<sup>3</sup>Department of Environment and Forests, Andaman and Nicobar, Van Sadan, Port Blair, India.



**Figure 1.** Tidal variation of CH<sub>4</sub>, N<sub>2</sub>O, salinity and percent O<sub>2</sub> saturation in Wright Myo mangrove creek waters during (a), dry season (January 2004); (b), wet season (July 2004).

 $k_w \perp \Delta p$ , where F is the gas flux (mol m<sup>-2</sup> d<sup>-1</sup>),  $k_w$  is the gas transfer velocity (cm hr<sup>-1</sup>), L is gas solubility (mol cm<sup>-3</sup> atm<sup>-1</sup>), and  $\Delta p$  is the water-to-air gas partial pressure difference. We derived  $k_w$  from a  $k_w$ -wind speed relation for CO<sub>2</sub> in estuaries [Clark et al., 1995]. We chose this because it takes better account of non-wind speed driven turbulence (e.g., tidal currents) than do alternative relations [e.g., Liss and Merlivat, 1986; Wanninkhof, 1992].

## 3. Results and Discussion

# 3.1. CH<sub>4</sub>, N<sub>2</sub>O, O<sub>2</sub> and Nutrient Dynamics

[7] The means and ranges of dissolved CH<sub>4</sub> and N<sub>2</sub>O concentrations during the dry season (mean CH<sub>4</sub> 491  $\pm$  133 nmol  $I^{-1}$ , range 282–704 nmol  $I^{-1}$ ; mean N<sub>2</sub>O 9.0  $\pm$  2.3 nmol  $I^{-1}$ , range 6.0–13.2 nmol  $I^{-1}$ ) did not differ significantly from those during the wet season (mean CH<sub>4</sub> 466  $\pm$  94 nmol  $I^{-1}$ , range 324–625 nmol  $I^{-1}$ ; mean N<sub>2</sub>O 8.6  $\pm$  1.3 nmol  $I^{-1}$ , range 6.6–10.5 nmol  $I^{-1}$ ); no seasonal trend was discernable for either CH<sub>4</sub> or N<sub>2</sub>O (Figure 1). This is consistent with mean water temperatures of 26.6  $\pm$  1.3°C (dry season) and 27.5  $\pm$  0.9°C (wet season); any seasonal thermal signal in methanogenesis or nitrification-denitrification rates was therefore minimal. The CH<sub>4</sub> and N<sub>2</sub>O concentrations correspond to saturations ~12,000–28,000% and ~102–208% respectively; hence Wright Myo mangrove surrounding waters are a potentially strong CH<sub>4</sub> source but a weaker N<sub>2</sub>O source to air throughout the year.

[8] During both surveys,  $CH_4$ ,  $N_2O$ ,  $NH_4^+$  and  $NO_3^-$  were more strongly (negatively) correlated with tidal height ( $r^2$ :  $CH_4 = 0.84$ ;  $N_2O = 0.94$ ) than with salinity ( $r^2$ :  $CH_4 = 0.80$ ;  $N_2O = 0.88$ ) (all: p < 0.001, n = 24). Given the lack of seasonality in  $CH_4$  and  $N_2O$  concentrations and the contrasting salinity ranges (dry season 20-27; wet season 0-28; Figure 1), tidal dilution apparently only negligibly affects dissolved gas concentrations at Wright Myo. Dissolved  $O_2$  gives insight into the controlling mechanisms (Figure 1). In the wet season (July) survey dissolved  $O_2$  was

on average supersaturated (mean 108 ± 16%, range 78-130%), whereas in the dry season (January) survey it was always undersaturated (mean  $49 \pm 6\%$ , range 41-61%) In both surveys percent  $O_2$  saturation (% $O_2$ ) deviated from that expected from diurnal primary production and respiration cycles (i.e., increase until sunset and then decrease until dawn). In July  $\%O_2$  was maximal prior to sunset (low tide). It initially decreased during the night but reached a minimum around high tide, 5-6 hours prior to sunrise (low tide). It then increased until about three hours after sunrise, after which it declined. In January %O2 followed an opposite trend; it declined to a minimum around sunset (low tide), increased to a maximum around midnight (high tide), declined to a minimum around sunrise (low tide), and then increased again (Figure 1). These data clearly include a tidal signal. During January the decrease in %O<sub>2</sub> toward low tide and its increase toward high tide are consistent with tidal pumping in which low-O<sub>2</sub> porewaters seep into the creek waters from surrounding mangrove sediments as hydrostatic pressure gradually falls and then rises [Ovalle et al., 1990]. Presumably during the July survey these effects were somewhat masked by high photosynthesis and respiration rates, and the torrential rain from around 0100 hours. During the rain salinity rapidly fell toward zero, much lower than during the previous low water, and it remained so for several hours (Figure 1). The increasing %O<sub>2</sub> between midnight high water and sunrise low water is not inconsistent with continued high night time respiration because the heavy rain could have effected significant reoxygenation, offsetting the impact of respiration on %O<sub>2</sub>. Tidal pumping of nutrients [Lara and Dittmar, 1999] and carbon system parameters [Borges et al., 2003] has been observed in other tidal mangroves.

[9] The dry season survey (January)  $NH_4^+$  contribution to total dissolved inorganic nitrogen (DIN) was high (Figure 2: mean  $82 \pm 2\%$ , range 79-87%) and similar to values in other mangrove ecosystems [*Lara and Dittmar*, 1999], whereas the wet season survey (July)  $NH_4^+$  contribution was more variable and lower (Figure 2: mean  $77 \pm 10\%$ ,

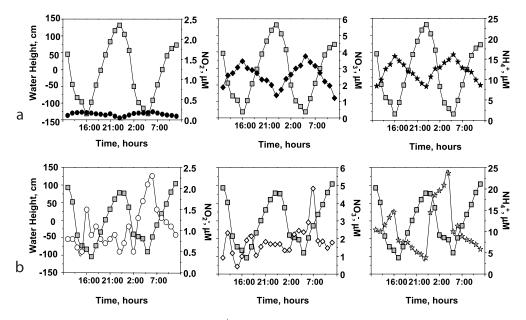


Figure 2. Tidal variation of dissolved inorganic  $NH_4^+$ ,  $NO_3^-$  and  $NO_2^-$  in Wright Myo mangrove creek waters during (a), dry season (January 2004); (b), wet season (July 2004).

range 58–93%). The rainfall during this survey actively mobilized the surface sediment and DIN rapidly increased to about twice its mean value over the previous 12 hours; the NH<sub>4</sub><sup>+</sup> fraction of DIN correspondingly increased to 88  $\pm$  3%. Both NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> also increased, but they lagged behind NH<sub>4</sub><sup>+</sup> by about 2 hours (Figure 2). When the rain ceased DIN began to decline. The NH<sub>4</sub><sup>+</sup> fraction of DIN also decreased but both NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> continued to increase before eventually declining toward their pre-rain values; the NO<sub>2</sub><sup>-</sup> peak was about 2–3 hours ahead of the NO<sub>3</sub><sup>-</sup> peak (Figure 2). This is consistent with nitrification of NH<sub>4</sub><sup>+</sup> mobilized from the sediment porewaters, to NO<sub>3</sub><sup>-</sup> via NO<sub>2</sub><sup>-</sup>.

[10] During and after the rain the anti-correlation between CH<sub>4</sub> and tidal height observed at other times was comparatively weak; CH<sub>4</sub> concentrations were apparently suppressed whereas N2O was apparently unaffected (Figure 1). This presumably indicates CH<sub>4</sub> oxidation during sediment surface mobilization. Turbidity increased abruptly from <100 mg l<sup>-1</sup> over the first 15 hours of the survey to  $270 \pm 130$  mg l<sup>-1</sup> during the rain; enhanced CH<sub>4</sub> oxidation has been demonstrated following clay mineral addition to methanotroph cultures [Weaver and Dugan, 1972]. Such conditions would also favor N2O production via nitrification of NH<sub>4</sub> [Goreau et al., 1980], consistent with the observed behavior of NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> (Figure 2) If on the other hand the N2O was mainly from denitrification it would have been suppressed by increased O2 during the rain, but there is no evidence for this (Figure 1). Other studies also indicate a predominantly nitrification source for mangrove N<sub>2</sub>O [Bauza et al., 2002; Munoz-Hincapie et al., 2002].

#### 3.2. CH<sub>4</sub> and N<sub>2</sub>O Emissions at Wright Myo

[11] Mangrove creek water CH<sub>4</sub> and N<sub>2</sub>O emissions derived from the *Clark et al.* [1995] relation (Table 1) are the means of hourly estimates over the full 24 hour surveys, whereas static (mangrove forest sediment-water-air emissions) and floating chamber (creek water emissions) data

(Table 1) were only collected for 2-3 hour periods. Chamber fluxes were therefore adjusted to take account of the strong diurnal signals in creek water CH<sub>4</sub> and N<sub>2</sub>O, in order to give representative mean fluxes for the full 24 hour surveys. We assumed the instantaneous water-to-air flux in each case to be proportional to the water-air partial pressure difference only; for the free-floating chamber this assumption is valid given that wind speeds were low and approximately constant during both seasons, hence flux variability related to short term changes in  $k_w$  can be discounted. For the static chamber it applies indirectly via the link between creek water gas content and tidal pumping due to hydrostatic pressure (tidal height); we assume that lateral creek water influx was minimal due to its inhibition by the chamber base collar. Mean creek water N<sub>2</sub>O concentrations during static chamber deployments were  $\sim 10\%$  higher (dry season) and  $\sim$ 5% higher (wet season) than over the full tidal cycles; to convert to 24-hour fluxes the chamber fluxes were adjusted downward by these amounts. Similarly, the dry season CH<sub>4</sub> flux was adjusted downward by  $\sim$ 13%, whereas the wet season flux was adjusted upward by  $\sim 30\%$  due to the rain-induced decline in creek water CH4 during deployment (Figure 1). We consider the precipitation event to have been atypical, hence our 24-hour estimate represents a wet season "dry" day. Floating chamber fluxes were

**Table 1.** CH<sub>4</sub> and N<sub>2</sub>O Emission Fluxes ( $\mu$ mol m<sup>-2</sup> hr<sup>-1</sup>) at Wright Myo; Observations During January 2004 (Dry Season) and July 2004 (Wet Season)

	Mangrove Creek			Mangrove Forest		
	Wet S	eason	Dry Season	Wet Season <sup>a</sup>	Dry Season <sup>a</sup>	
$N_2O$	1.3 <sup>b</sup>	0.23°	0.24 <sup>c</sup>	0.21	0.12	
$CH_4$	34.5 <sup>b</sup>	$23.0^{c}$	23.9°	17.8	28.8	

<sup>&</sup>lt;sup>a</sup>Static chamber estimates.

<sup>&</sup>lt;sup>b</sup>Floating chamber estimates.

<sup>&</sup>lt;sup>c</sup>Estimated from the Clark et al. [1995] relation.

Table 2. CH<sub>4</sub> and N<sub>2</sub>O Emission Fluxes (μmol m<sup>-2</sup> hr<sup>-1</sup>) From Mangrove Ecosystems<sup>a</sup>

	Emission, μmol m <sup>-2</sup> hr <sup>-1</sup>			
Site	Location	$N_2O$	CH <sub>4</sub>	Reference
Queensland, Australia		(-0.1)-0.3	1 - 22	Kreuzwieser et al. [2003]
NE Hainan I. China	$(\sim 19^{\circ} \text{N} \ 110^{\circ} \text{E})$		0.9 - 2.8	Lu et al. [1999]
Jiulonjiang Estuary, China	(~24°N 117°E)	0 - 200	0 - 100	Alongi et al. [2005]
SW India	$(\sim 11 - 13^{\circ} \text{N } 79^{\circ} \text{E})$		125 - 813	Purvaja and Ramesh [2001]
Pichavarum/Cauvery Deltas, SW India	(~11°N 79°E)		21 - 67	Purvaja et al. [2004]
SW Puerto Rico	$(\sim 18^{\circ} \text{N } 67^{\circ} \text{W})$		10 - 215	Sotomayor et al. [1994]
SW Puerto Rico	$(\sim 18^{\circ} \text{N } 67^{\circ} \text{W})$	0.1 - 7.8		Corredor et al. [1999]
SW Puerto Rico	$(\sim 18^{\circ} \text{N } 67^{\circ} \text{W})$	0.05 - 1.4		Bauza et al. [2002]
SW Puerto Rico	$(\sim 18^{\circ} \text{N } 67^{\circ} \text{W})$	0.05		Munoz-Hincapie et al. [2002]
Mtoni Mangrove, Tanzania	(~6°S 39°E)		(-0.8) - 520	Lyimo et al. [2002]
Ranong Province, Thailand	$(\sim 10^{\circ} \text{N } 98^{\circ} \text{E})$		12 - 33	Lekphet et al. [2005]
Wright Myo, Andaman Is	(~12°N 93°E)	0.1 - 1.3	18-35	This Study

<sup>a</sup>All fluxes excepting some of those in this work were estimated using static chambers; the negative emissions in parentheses indicate a net flux into the mangrove sediment.

corrected based on creek water data for the first 12 hours of the survey only, ignoring the post-rain data; for both gases the required adjustments were  $\sim\!10\%$ . For  $N_2O$ , which was apparently not measurably affected by the rain (Figure 1), adjusting the floating chamber flux over the full 24 hours did not change this outcome. The discrepancy in required adjustments between the static and floating chambers relates to their being deployed at different times.

[12] During both surveys we observed periodic bubble ebullition, which was most intense around low tide. Hydrostatic pressure changes of a few percent can significantly increase ebullition [Ostrovsky, 2003], and increased sediment shear stress also contributes [Joyce and Jewell, 2003]. CH<sub>4</sub> ebullition can exceed diffusional/turbulent exchange in shallow systems by more than an order of magnitude [Ostrovsky, 2003], and it can be significant for other gases via diffusion into the bubbles [Leifer and Patro, 2002]. The flux estimates (Table 1) therefore likely represent minimum values.

[13] Creek water fluxes estimated with the Clark et al. [1995] relation showed no seasonality, consistent with the concentration data (Figure 1) and the insensitivity of  $k_w$  to the low ambient wind speed ranges encountered (wet season,  $4.2 \pm 1.0 \text{ m s}^{-1}$ ; dry season  $2.0 \pm 0.5 \text{ m s}^{-1}$ ). At these wind speeds alternative widely used relations underestimate [Liss and Merlivat, 1986] or overestimate [Wanninkhof, 1992]  $k_w$  measured in tidal estuaries with gaseous tracers [Clark et al., 1995]. CH4 emissions were about 100 times higher than those of N<sub>2</sub>O. Creek water fluxes determined with the floating chamber were 1.5 times higher for CH<sub>4</sub> and  $\sim$ 5.5 times higher for N<sub>2</sub>O than these wind speed based estimates (Table 2). Some authors have found floating chambers to overestimate gas exchange relative to other methods [Clark et al., 1995; Raymond and Cole, 2001], however others find much closer agreement [Kremer et al., 2003]. Although the intense rain during deployment could have suppressed wind waves at the low wind speeds encountered, strong rain-enhancement of gas exchange via increased surface turbulence and surface bubble entrainment is well known [Ho et al., 2000]. Bubble entrainment increases with rain intensity and drop size but overall surface turbulence effects dominate, accounting for about 80% of the total enhancement for low solubility gases [Ho et al., 2000]. Based on our rainfall estimate and laboratory data [Ho et al., 2000] kw enhancement of the

order observed is not unlikely. Given the small rainenhancement of  $CH_4$  exchange relative to  $N_2O$ , this supports our hypothesis of creek water  $CH_4$  oxidation and the corresponding changes to DIN speciation during intense rainfall (Figure 1). Mangrove forest sediment  $CH_4$  fluxes are also consistent with this hypothesis, being  ${\sim}40\%$  lower during the wet season survey (Table 2). In contrast the wet season survey forest sediment  $N_2O$  flux was about twice as high as the dry season survey flux. This may reflect additional  $N_2O$  production in the sediments via the nitrification of  $NH_4^+$ , as implied by the DIN data (Figure 1).

[14] There are few available estimates of N<sub>2</sub>O or CH<sub>4</sub> emissions from mangrove ecosystems (Table 2) and none of these considers the contribution from surrounding creek waters, even though at Wright Myo this is comparable per unit area to the flux from mangrove sediment (Table 1). Our N<sub>2</sub>O and CH<sub>4</sub> emissions estimates for Wright Myo are toward the low end of previously published ranges for mangroves (Table 2). These span two orders of magnitude; however the data include both anthropogenically impacted and pristine sites. For example, the Jiulonjiang estuary, China, [Alongi et al., 2005] is highly urbanized, high CH<sub>4</sub> emissions for SW Puerto Rico [Sotomayor et al., 1994] and SE India [Purvaja and Ramesh, 2001] reflect domestic sewage pollution, and the N<sub>2</sub>O emissions for SW Puerto Rico reflect anthropogenic N addition [Corredor et al., 1999]. Overall mangrove ecosystems appear to be a larger source of CH<sub>4</sub> than N<sub>2</sub>O to the atmosphere (Table 2).

# 3.3. Global Fluxes of $CH_4$ and $N_2O$ from Mangrove Ecosystems

[15] Given the relatively low CH<sub>4</sub> and N<sub>2</sub>O emissions from pristine Wright Myo (Table 2), up scaling these based on estimated global areas of mangrove forest and creek enables a conservative estimate of the CH<sub>4</sub> and N<sub>2</sub>O source strengths for mangrove ecosystem worldwide, the first such estimate to include the contributions from both mangrove forest and surrounding creek waters. For this we assume worldwide mangrove forest and creek areas  $\sim 0.2 \times 10^6 \text{ km}^2$  and  $\sim 0.36 \times 10^6 \text{ km}^2$  respectively [Borges et al., 2003; Selvam, 2003], and similar wet and dry season floating chamber fluxes based on measured creek water concentrations and wind speeds. Worldwide mangrove ecosystem emissions to the atmosphere are thus  $\sim 13 \times 10^{10}$  mol CH<sub>4</sub> yr<sup>-1</sup> (2.2  $\times$  10<sup>12</sup> g yr<sup>-1</sup>) and 2.7  $\times$ 

 $10^9$  mol  $N_2O$  yr $^{-1}$  ( $1.2 \times 10^{11}$  g  $N_2O$  yr $^{-1}$ ). Previously estimated worldwide estuarine emissions are  $\sim 5-8 \times 10^{10}$  mol  $CH_4$  yr $^{-1}$  and  $\sim 8-13 \times 10^{10}$  mol  $N_2O$  yr $^{-1}$  [Bange et al., 1994, 1996]. Even though our emission flux estimates for Wright Myo are conservative relative to data from other mangroves (Table 2) and exclude the potential ebullition contribution for  $CH_4$ , they nevertheless imply that  $CH_4$  fluxes from mangrove ecosystems could dominate  $CH_4$  emissions from coastal ecosystems worldwide, and that previous work may have seriously underestimated the magnitude of this flux. By contrast, mangrove ecosystems appear to be relatively small contributors to the net global flux of atmospheric  $N_2O$  from coastal sites.

[16] It is instructive to examine the potential net greenhouse gas budget of mangrove ecosystems by comparing our CH<sub>4</sub> and N<sub>2</sub>O flux estimates with the available data for CO<sub>2</sub>. There are currently no simultaneously derived CO<sub>2</sub> flux estimates for mangrove forest and creek waters, and no simultaneous measurements of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O fluxes for either environment. The available CO<sub>2</sub> data for creek waters imply net heterotrophy and an atmospheric  $CO_2$  source  $\sim 50 \times 10^{12}$  g C y<sup>-1</sup>; this is based on a creek water area  $\sim 0.2 \times 10^6$  km<sup>2</sup> [Borges et al., 2003] which may be an underestimate [Selvam, 2003]. Even so, assuming that  $\sim$ 75% of the total carbon flux into mangrove ecosystems is respired and re-emitted as  $CO_2$  with only  $\sim 2-3\%$  carbon burial in sediments, globally mangrove ecosystems (forest and creek) may be a small net sink for atmospheric CO<sub>2</sub>  $\sim 18 \times 10^{12} \text{ g C y}^{-1}$  [Alongi, 2002]. Based on this and taking into account means of 20-year and 100-year global warming potentials of 286 for N<sub>2</sub>O and 43 for CH<sub>4</sub> [Intergovernmental Panel on Climate Change, 2001], mangroves could be an overall small greenhouse gas source to the troposphere equivalent to  $\sim 100 \times 10^{12}$  g CO<sub>2</sub> y<sup>-1</sup>. However, uncertainty in this estimate is inherently large because source data remain very scarce.

[17] New data for N<sub>2</sub>O and CH<sub>4</sub> reported here raise an important question: what is the overall role of mangrove ecosystems in the greenhouse gas budget of the troposphere? The inherent uncertainty of our estimate herein derived highlights a need for further detailed study. Although the direct addition of carbon and nitrogen to mangrove ecosystems demonstrably leads to enhanced emissions of N<sub>2</sub>O and CH<sub>4</sub> [Purvaja and Ramesh, 2001; Munoz-Hincapie et al., 2002], wholesale mangrove clearance on the other hand may result in net heterotrophy and accelerated emissions of CO<sub>2</sub> [Alongi et al., 2004]. Understanding and evaluating the balance of these processes is highly topical, being relevant to evaluating the efficacy of proposed CO<sub>2</sub> mitigation strategies that involve mangrove replanting, for example. Additional data are therefore required from a range of mangrove ecosystems to better constrain the net consequences of these effects. Future studies could usefully focus on comparing emissions from similar sites with and without mangroves, emissions before and after mangrove plantation, and emissions from established and eroding mangrove sites.

[18] **Acknowledgments.** The authors thank the authorities of the Forest Department of Andaman and Nicobar Administration and colleagues at the Institute of Ocean Management, Anna University, for their assistance with sampling. This work was funded by the U.K. Natural Environment

Research Council (grant NER/A/S/2001/00507: Nitrification, denitrification and nitrous oxide in Indian mangrove ecosystems).

#### References

Alongi, D. M. (2002), Present state and future of the world's mangrove forests, *Environ. Conserv.*, 29, 331–349.

Alongi, D. M., A. Sasekumar, V. C. Chong, J. Pfitzner, L. A. Trott, F. Tirendi, P. Dixon, and G. J. Brunskill (2004), Sediment accumulation and organic material flux in a managed mangrove ecosystem: Estimates of land-ocean-atmosphere exchange in peninsular Malaysia, *Mar. Geol.*, 208, 383–402.

Alongi, D. M., J. Pfitzner, L. A. Trott, P. Dixon, and D. W. Klumpp (2005), Rapid sediment accumulation and microbial mineralization in forests of the mangrove Kandelia candel in the Jiulongjiang estuary, China, *Estuar-ine Coastal Shelf Sci.*, 63, 605–618.

Bange, H. W., U. H. Bartell, S. Rapsomanikis, and M. O. Andreae (1994), Methane in the Baltic and North Seas and a reassessment of the marine emissions of methane, *Global Biogeochem. Cycles*, 8, 465–480.

Bange, H. W., S. Rapsomanikis, and M. O. Andreae (1996), Nitrous oxide in coastal waters, *Global Biogeochem. Cycles*, 10, 197–207.

Bauza, J. F., J. M. Morell, and J. E. Corredor (2002), Biogeochemistry of nitrous oxide production in the Red Mangrove *Rhizophora mangle* forest sediments, *Estuarine Coastal Shelf Sci.*, 55, 697–704.

Borges, A. V., S. Djenidi, G. Lacroix, J. Théate, B. Delille, and M. Frankignoulle (2003), Atmospheric CO<sub>2</sub> flux from mangrove surrounding waters, *Geophys. Res. Lett.*, 30(11), 1558, doi:10.1029/2003GL017143.

Clark, J. F., P. Schlosser, H. J. Simpson, M. Stute, R. Wanninkhof, and D. T. Ho (1995), Relationship between gas transfer velocities and wind speeds in the tidal Hudson River determined by a dual tracer technique, in *Air-Water Gas Transfer*, edited by B. Jahne and E. C. Monahan, pp. 785–800, Aeon Verlag and Studio, Hanau, Germany.

Corredor, J. E., J. M. Morell, and J. F. Bauza (1999), Atmospheric nitrous oxide fluxes from mangrove sediments, *Mar. Pollut. Bull.*, 38, 473–478. Dittmar, T., N. Hertkorn, G. Kattner, and R. J. Lara (2006), Mangroves, a major source of dissolved organic carbon to the oceans, *Global Biogeochem. Cycles*, 20, GB1012, doi:10.1029/2005GB002570.

Goreau, T. J., W. A. Kaplan, S. C. C. Wofsy, M. B. McElroy, F. W. Valois, and S. W. Watson (1980), Production of NO<sub>2</sub> and N<sub>2</sub>O by nitrifying bacteria at reduced concentrations of oxygen, *Appl. Environ. Microbiol.*, 40, 526–532.

Ho, D. T., W. E. Asher, L. F. Bliven, P. Schlosser, and E. L. Gordan (2000), On mechanisms of rain-induced air-water gas exchange, *J. Geophys. Res.*, 105, 24,045–24,058.

Intergovernmental Panel on Climate Change (2001), Climate Change 2001: The Scientific Basis: Contribution to Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change, edited by J. T. Houghton et al., 881 pp., Cambridge Univ. Press. New York.

J. T. Houghton et al., 881 pp., Cambridge Univ. Press, New York. Joyce, J., and P. W. Jewell (2003), Physical controls on methane ebullition from reservoirs and lakes, *Environ. Eng. Geosci.*, 9, 167–178.

Kremer, J. N., S. W. Nixon, B. Buckley, and P. Roques (2003), Technical note: Conditions for using the floating chamber method to estimate airwater gas exchange, *Estuaries*, 26, 985–990.

Kreuzwieser, J., J. Buchholz, and H. Rennenberg (2003), Emission of methane and nitrous oxide by Australian mangrove ecosystems, *Plant Riol* 5, 423–431

Lara, R. J., and T. Dittmar (1999), Nutrient dynamics in a mangrove creek (North Brazil) during the dry season, *Mangroves Salt Marshes*, 3, 185–105

Leifer, I., and R. K. Patro (2002), The bubble mechanism for methane transport from the shallow sea bed to the surface: A review and sensitivity study, *Cont. Shelf Res.*, 22, 2409–2428.

Lekphet, S., S. Nitisoravut, and S. Adsavakulchai (2005), Estimating methane emissions from mangrove area in Ranong Province, Thailand, *Songklanakarin J. Sci. Technol.*, 27, 153–163.

Liss, P. S., and L. Merlivat (1986), Air-sea gas exchange rates: Introduction and synthesis, in *The Role of Air-Sea Exchange in Geochemical Cycling*, edited by P. Buat-Menard, pp. 113–127, Springer, New York.

Lu, C. Y., Y. S. Wong, N. F. Y. Tam, Y. Ye, and P. Lin (1999), Methane flux and production from sediments of a mangrove wetland on Hainan Island, China, *Manage. Saltmarsh*, 3, 41–49.

Lyimo, T. J., A. Pol, and H. J. M. Op Den Camp (2002), Methane emission, sulphide concentration and redox potential profiles in Mtoni mangrove sediment, Tanzania, *Western Indian Ocean J. Mar. Sci.*, 1, 71–80.

Munoz-Hincapie, N., J. M. Morell, and J. E. Corredor (2002), Increase of nitrous oxide flux to the atmosphere upon nitrogen addition to red mangroves sediments, *Mar. Pollut. Bull.*, 44, 992–996.

Ostrovsky, I. (2003), Methane bubbles in Lake Kinneret: Quantification and temporal and spatial heterogeneity, *Limnol. Oceanogr.*, 48, 1030–1036

- Ovalle, A. R. C., C. E. Rezende, L. D. Lacerda, and C. A. R. Silva (1990), Factors affecting the hydrochemistry of a mangrove creek, Sepetiba Bay, Brazil, *Estuarine Coastal Shelf Sci.*, 31, 639–650.
- Purvaja, R., and R. Ramesh (2001), Natural and anthropogenic methane emission from wetlands of south India, *Environ. Manage.*, 27, 547–557.
- Purvaja, R., R. Ramesh, and P. Frenzel (2004), Plant-mediated methane emission from an Indian mangrove, *Global Change Biol.*, 10, 1825–1834.
- Raymond, P. A., and J. J. Cole (2001), Gas exchange in rivers and estuaries: Choosing a gas transfer velocity, *Estuaries*, 24, 312–317.
- Selvam, V. (2003), Environmental classification of mangrove wetlands of India, *Curr. Sci.*, 84, 759–765.
- Sotomayor, D., J. E. Corredor, and J. M. Morell (1994), Methane flux from mangrove sediments along the Southwestern Coast of Puerto Rico, *Estuaries*, *17*, 140–147.
- Upstill-Goddard, R. C., A. P. Rees, and N. J. P. Owens (1996), Simultaneous high-precision measurements of methane and nitrous oxide in

- water and seawater by single-phase equilibration gas chromatography, *Deep. Sea. Res., Part I, 43*, 1669–1682.
- Wanninkhof, R. (1992), Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.*, 97, 7373–7382.
- Weaver, T. L., and P. R. Dugan (1972), Enhancement of bacterial methane oxidation by clay minerals, *Nature*, 237, 518-519.
- J. Barnes, R. Upstill-Goddard, and G. Uher, Ocean Research Group, School of Marine Science and Technology, University of Newcastle upon Tyne, Newcastle Upon Tyne NE1 7RU, UK. (rob.goddard@ncl.ac.uk)
- K. Krithika, A. Nirmal Rajkumar, R. Purvaja, R. Ramesh, and B. Senthil Kumar, Institute for Ocean Management, Anna University, Chennai 600 025, India.
- K. Ravichandran, Department of Environment and Forests, Andaman and Nicobar, Van Sadan, Haddo P.O., Port Blair 744 102, India.