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Carbon Dioxide and Methane Emissions from Mangrove-Associated Waters of the Andaman Islands, Bay of Bengal

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Abstract We estimated CO_2 and CH_4 emissions from mangrove-associated waters of the Andaman Islands by sampling hourly over 24 h in two tidal mangrove creeks (Wright Myo; Kalighat) and during transects in contiguous shallow inshore waters, immediately following the northeast monsoons (dry season) and during the peak of the southwest monsoons (wet season) of 2005 and 2006. Tidal height correlated positively with dissolved O_2 and negatively with pCO_2, CH_4, total alkalinity (TAlk) and dissolved inorganic carbon (DIC), and pCO_2 and CH_4 were always highly supersaturated (330–1,627 % CO_2; 339–26,930 % CH_4). These data are consistent with a tidal pumping response to hydrostatic pressure change. There were no seasonal trends in dissolved CH_4 but pCO_2 was around twice as high during the 2005 wet season than at other times, in both the tidal surveys and the inshore transects. Fourfold higher turbidity during the wet season is consistent with elevated net benthic and/or water column heterotrophy via enhanced organic matter inputs from adjacent mangrove forest and/or the flushing of CO_2-enriched soil waters, which may explain these CO_2 data. TAlk/DIC relationships in the tidally pumped waters were most consistent with a diagenetic origin of CO_2 primarily via sulphate reduction, with additional inputs via aerobic respiration. A decrease with salinity for pCO_2, CH_4, TAlk and DIC during the inshore transects reflected offshore transport of tidally pumped waters. Estimated mean tidal creek emissions were ~23–173 mmol m^{-2} day^{-1} CO_2 and ~0.11–0.47 mmol m^{-2} day^{-1} CH_4. The CO_2 emissions are typical of mangrove-associated waters globally, while the CH_4 emissions fall at the low end of the published range. Scaling to the creek open water area (2,700 km^2) gave total annual creek water emissions ~$3.6–9.2\times10^{10}$ mol CO_2 and $3.7–34\times10^7$ mol CH_4. We estimated emissions from contiguous inshore waters at ~1.5×10^{11} mol $CO_2 year^{-1}$ and 2.6×10^8 mol $CH_4 year^{-1}$, giving total emissions of ~1.9×10^{11} mol $CO_2 year^{-1}$ and ~3.0×10^8 mol $CH_4 year^{-1}$ from a total area of mangrove-influenced water of ~3×10^4 km^2. Evaluating such emissions in a range of mangrove environments is important to resolving the greenhouse gas balance of mangrove ecosystems globally. Future such studies should be integral to wider quantitative process studies of the mangrove carbon balance.

Keywords Mangrove ecosystems · Tidal pumping · pCO_2 · CH_4 · O_2 · Talk · DIC · Emission fluxes

Introduction

Continental shelves cover only 8 % of the ocean surface but they play a major role in marine biogeochemistry. Large nutrient fluxes from rivers and upwelling and high rates of organic matter remineralisation arising from benthic–pelagic coupling lead to much higher primary productivity than in the open ocean (Wollast 1998; Muller-Karger et al. 2005). Consequently, they are considered overall net sinks for tropospheric CO_2, equivalent to perhaps as much as 25–60 % of the open ocean CO_2 sink (Borges et al. 2005). Conversely, near-shore upwelling regions, estuaries, coral reefs and salt marsh and mangrove waters together constitute a net source to the atmosphere, not only of CO_2 but also of CH_4 (Borges et al. 2005; Bange 2006). The emissions are both high and

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uncertain, the uncertainty reflecting a regional data bias favouring studies in northern temperate locations.

Mangrove ecosystems cover ~1.4×10^5 km^2 of the global intertidal area, equivalent to ~0.7 % of the total area of tropical forest (Giri et al. 2011). Nevertheless, they are among the world's most productive biomes, accounting for ~11 % of the total terrestrial carbon flux and ~10 % of the terrestrial dissolved organic carbon flux, to the oceans (Jennerjahn and Ittekot 2002; Dittmar et al. 2006). Their overall status is net autotrophic (Alongi 2002), mangrove plant biomass both above and belowground accounting for around 15 % of organic carbon sequestration by contemporary marine sediments (Jennerjahn and Ittekot 2002). Even so, mangrove sediments and their overlying waters are widely considered to be net heterotrophic (Gattuso et al. 1998), reflecting large and variable organic carbon inputs from diverse sources such as mangrove and terrestrial detritus, microphytobenthos, phytoplankton and sea grasses (Bouillon and Boschker 2006). Consequently, mangrove surrounding waters have been shown to emit large amounts of CO_2 and CH_4 to the atmosphere (e.g., Borges et al. 2003; Barnes et al. 2006; Ramesh et al. 2007; Bouillon et al. 2007b; Bouillon et al. 2008; Koné and Borges 2008). Indeed, Chen and Borges (2009) estimate mangrove surrounding waters to emit around 0.05 Pg C annually as CO_2, about 9–18 % of the total coastal source (estuaries, salt marshes and mangroves) of 0.28–0.57 Pg C year^{-1} and Barnes et al. (2006) suggest that mangrove surrounding waters could be the dominant coastal CH_4 source. Given a net shelf CO_2 sink of ~0.33–0.36 Pg C year^{-1} (Chen and Borges 2009) quantifying mangrove emissions of gaseous carbon is important for better constraining the carbon budgets of tropical continental margins.

This paper analyses the seasonal (southwest and northeast monsoons) distributions of pCO_2, dissolved CH_4 and O_2, total alkalinity (TAlk) and dissolved inorganic carbon (DIC) over 24-h cycles in two pristine mangrove creeks and in adjacent inshore surface water transects in the Andaman Islands, Bay of Bengal. In addition, annual CO_2 and CH_4 emissions were derived from these mangrove waters and using these and other data, the global carbon balance of mangrove ecosystems was briefly re-examined.

Materials and Methods

Study Area

The Andaman Islands are an archipelago of more than 550 islands (524 uninhabited) covering 6,408 km^2 of the south-eastern Bay of Bengal and extending north-south for 360 km between latitudes 6–14° N and 92–94° E (Fig. 1). Subsoils derive mainly from argillaceous and algal limestone and climate is humid tropical with a relative humidity of 70–90 %. Temperature is rather constant with minima of 24–25 °C and maxima of 27–30 °C during all months; there is no discernable winter season (Singh et al. 1987). Mean annual precipitation is ~314 cm and monthly precipitation is maximal (~60 cm) at the peak of the south west monsoon (June–September) and minimal (<5 cm) between January and April (Singh et al. 1987). There is only one river, the Kalpong, which discharges to north-west North Andaman Island (Selvam 2003). Around 86 % of the total land area is covered by rainforest, some of which has been cleared for commercial plantation and agricultural use, leading to localised decreases in soil pH and organic content (Dagar et al. 1995).

Mangrove forest, which covers 892 km^2 (~0.6 % of the global total) and fringes around one quarter of the 1,900-km coastline, is among the world's most pristine. Mangrove species diversity and biomass is high, reflecting the high rainfall amount and frequency. Some 24 mangrove species are present, of which *Rhizophora apiculata*, *Rhizophora mucronata* and *Ceriops tagal* dominate (Selvam 2003). Around 255 km^2 of the mangrove forest is described as "dense" with the remainder listed as "moderately dense" or "open" (Forest Survey of India 2005). Mangrove clearance for agriculture, aquaculture and domestic and industrial development is significant and is increasing, causing soil erosion and the loss of organic matter and nutrients from some locations (Singh et al. 1986). Mangrove-associated open water totals at ~2,700 km^2; this is around three times the area occupied by mangrove forest and is 2 % of the global estimate of 0.15×10^6 km^2 for open mangrove waters (Borges et al. 2005). The tidal range in Andaman open mangrove waters is 1.90 m (Selvam 2003), and the diurnal range in salinity is around 5–25 at the peak of the wet season (July–August) and 10–34 at the end of the dry season (March–April). Local times of sunrise and sunset are around 05.10 and 17.30 hours respectively, throughout the year.

Sampling and Analytical Techniques

Surveys of 24-h duration were conducted, commencing at midday (around 7 h after sunrise) with hourly surface water sampling for pH, TAlk, dissolved CH_4 and O_2, turbidity, salinity and temperature, at fixed locations in two tidal mangrove creeks: Wright Myo (11°47′27.7″ N, 92°42′24.3″ E), South Andaman, which is 8 km long and 20–40 m wide dependant on tidal state and Kalighat (13°07′30.7″ N; 92°56′48.2″ E), North Andaman, which is 10 km long and has a mean width of ~100 m (Fig. 1). Wright Myo was surveyed at the beginning of the inter-monsoon period immediately following the northeast monsoon, on 14–15 April 2005 and 21–22 April 2006 ("dry season") and during the peak of the southwest monsoon, on 22–23 August 2005 and 24–25 August 2006 ("wet season"). During 2004, this site was surveyed similarly for CH_4 and N_2O, as reported elsewhere (Barnes et al. 2006).

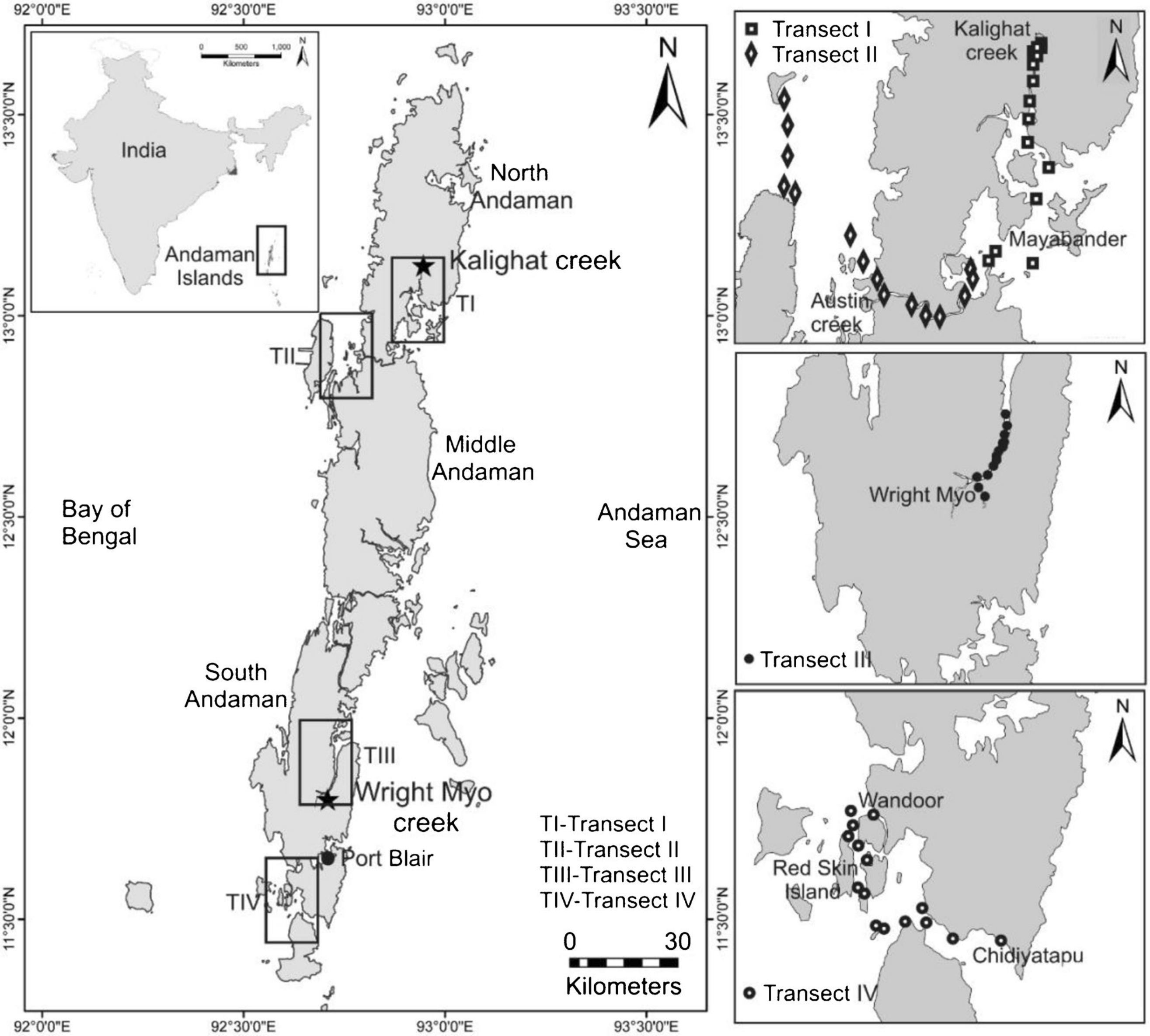

Fig. 1 Locations of Kalighat and Wright Myo tidal surveys and the surface water transects: *TI* Kalighat to Mayabander, *TII* Mayabander to Interview Island via Austin creek, *TIII* Wright Myo to the Andaman Sea and *TIV* Wandoor National Park to Chidiyatapu

Kalighat was surveyed on 11–12 April 2005 (inter-monsoon: "dry season") and on 17–18 August 2005 (southwest monsoon: "wet season"). Additionally, wet and dry season surface water transects were carried out for pH, TAlk and CH_4 across ambient salinity ranges between mangroves and adjacent shallow near shore waters: TI and TII during April and August 2005 and TIII and TIV during both April and August 2005 and April and August 2006 (Fig. 1). TI covered ~18 km between Kalighat Creek (water depth ~1 m) and Mayabander (water depth ~10 m), TII covered ~28 km from Mayabander to Interview Island (maximum water depths ~5–10 m) via Austin creek (coral reef; maximum water depth ~20 m), TIII was a 9-km survey along and just offshore of Wright Myo (maximum water depth ~3-5 m) and TIV covered ~47 km from Wandoor National Park to Chipiyatapu (open water coral reef and fringing mangroves; maximum water depth ~15 m), through a channel connecting the Bay of Bengal to the Andaman Sea (Fig. 1).

Water samples were collected manually from 0.2 m depth (Richter & Wiese 2.5-L water sampler). Subsamples for dissolved CH_4 analysis were transferred into 100 mL glass bottles via silicon tubing with the careful exclusion of air bubbles, poisoned with 0.1 mL saturated $HgCl_2$ and sealed to leave no headspace. Analysis of CH_4 was by single-phase equilibration gas chromatography (GC) with a routine analytical precision (1 σ) of ±1 % (Upstill-Goddard et al. 1996). Method calibration was with certified gas standards of 6.74 and 12.5 ppmv CH_4 in N_2 (National Physical Laboratory, New Delhi, India). Considering logistical constraints, pH was not determined in situ. Instead, pH and TAlk subsamples were decanted into 100 mL pre-combusted glass bottles, poisoned with 0.1 mL of saturated $HgCl_2$ solution and sealed. Following transfer to the laboratory, they were stored in a refrigerator at 4 °C and subsequently allowed to equilibrate to room temperature (25 °C) prior to analysis. Corrections to in situ temperature were made as appropriate. The total time between sampling and analysis was always less than 4 days. TAlk was determined by electro-titration (Gran 1952), and pH was measured with a combination electrode (ORION) calibrated with NBS standard pH buffers. Typical reproducibility (1 σ) of TAlk and pH measurements was, respectively, ±4 μeq kg^{-1} and ±0.005. CO2Sys software (Pierrot et al. 2006) was used to calculate pCO_2 from pH, TAlk, temperature and salinity, adopting a protocol for waters of varying salinity (Frankignoulle and Borges 2001) and using the dissociation constants of Millero et al. (2006). On samples from three of the tidal surveys (Kalighat and Wright Myo, August 2005; Wright Myo, April 2006), cross-checking was made on these pCO_2 estimates by incorporating a methaniser (nickel catalyst at 250 °C in H_2) in the GC system to convert CO_2 to CH_4. Linear correlation of the data yielded: pCO_2 (GC)=0.936 pCO_2 (pH–TAlk)+397.8 (r^2=0.941, n=72). The offset is primarily a result of progressive divergence in the liquid junction potential between buffer and sample towards higher salinities (Frankignoulle and Borges 2001). Consequently, its effect is minimal at high pCO_2 and low salinity, typically being around 0.25 % at pCO_2>6,000 μatm but progressively increasing to around 3.6 % at pCO_2=3,000 μatm and around 13 % at pCO_2<2,000 μatm. Nevertheless, the likely range in pCO_2 was considered to be sufficiently wide so as to preclude these inherent errors from materially affecting our subsequent data interpretation. For consistency, only those survey pCO_2 data derived from pH and TAlk are discussed in this paper as these are the only complete pCO_2 data set for our samples. Salinity, temperature, turbidity and dissolved O_2 were determined in situ with a pre-calibrated multi-parameter probe (Horiba W-22.23). Precisions (1 σ) were ±0.01 salinity, ±0.2 °C, ±3 % turbidity and ±0.01 mg $O_2 L^{-1}$. Probe measurements of dissolved O_2 were routinely cross-checked by collecting two samples in every five for standard Winkler titration. The two methods gave satisfactory agreement: O_2 (probe)=0.992 O_2 (Winkler)−0.02 (r^2=0.959, n=61). Wind speed was recorded with a hand-held cup anemometer at 1 m height (Lutron LM8000; resolution±0.1 m s^{-1}); 1 min means were subsequently converted to equivalent 10 m values (Amorocho and DeVries 1980). Water depths and mid-depth water current velocities were measured hourly (open channel flow meter, Valeport, UK) for all tidal surveys. In addition, gas bubbles effusing from Wright Myo creek sediments on 21 April 2006 were collected. Samples were captured over a 2-h period spanning the first low tide (1700–1900 hours), in a gas-tight syringe with an integral luer needle connected to an inverted glass funnel with a septum at the base of its stem. Samples were transferred to gas-tight vacutainers for subsequent gas chromatographic analysis of CO_2 and CH_4 as described above.

Sea-to-air emission fluxes (F) of CO_2 and CH_4 were estimated using $F=k_w\ L\ \Delta p$, where k_w is the gas transfer velocity (in centimetres per hour), L is the Ostwald solubility coefficient and Δp is the partial pressure difference (in atmospheres) across the air–water interface. Values of L were from Weiss (1974) for CO_2 and Weisenburg and Guinasso (1979) for CH_4. k_w was estimated from the 10-m-derived wind speeds using the empirical k_w—wind speed relations of Clark et al. (1995) and Borges et al. (2004) for CO_2. Both were derived for use in shallow coastal waters where tidal current interaction with the seabed generates turbulence additional to that due to wind speed alone; the latter formally includes expressions for tidal current velocities and water depth, which is considered to be more applicable here than some other more commonly used relations (e.g., Liss and Merlivat 1986; Wanninkhof 1992). k_w for CO_2 was scaled to k_w for CH_4 using Schmidt numbers given in Wanninkhof (1992).

Results and Discussion

Creek Water Carbon During Tidal Surveys

Means and ranges of hourly pCO_2, CH_4, TAlk, DIC, O_2, salinity and turbidity are given in Table 1. Mean CH_4 did not differ significantly between dry and subsequent wet season surveys or in the case of Wright Myo, between consecutive years (mean of all samples, 349±125 nmol L^{-1}; 15,960±5,930 % saturation). Similarly, there was no significant seasonal variation in pCO_2 at Wright Myo (mean of all samples, 3,409±919 μatm; 903±243 % saturation). Previously, no seasonal variability in either CH_4 or N_2O at Wright Myo (Barnes et al. 2006) was found to be consistent with a negligible thermal effect on methanogenesis or nitrification/denitrification rates. Mean water temperatures were: dry season, 28.0±1.0 °C (range, 25.5–30.2 °C); wet season, 27.6±0.9 °C (range, 26.0–29.4 °C). By contrast, pCO_2 at Kalighat was around twice as high in the wet season than in the dry season and dissolved O_2 saturations were correspondingly lower (Table 1). These data are consistent with a wet season increase in net benthic and/or water column heterotrophy at Kalighat, perhaps reflecting enhanced organic matter inputs from adjacent mangrove forest and/or the flushing of soil waters enriched in CO_2 by respiration, as inferred previously for mangrove surrounding waters (Koné and Borges 2008). The observed three- to four-fold higher turbidity during the wet seasons (Table 1) is consistent with an enhanced organic matter flux and would

Table 1 Means (all: n=24) and ranges (in *brackets*) of biogeochemical variables measured hourly in Andaman mangrove creek waters

Site/date	Season	pCO_2 (μatm)	pCO_2 (% saturation)	CH_4 (nmol L^{-1})	CH_4 (% saturation)	TAlk (mmol L^{-1})	DIC (mmol L^{-1})	O_2 (% saturation)	Salinity	Turbidity (mg L^{-1})
Kalighat										
April 2005	Dry	2,180±382 (1,704–3,392)	574±101 (448–893)	421±106 (154–603)	9,283±4,248 (7,956–26,419)	2.61±0.15 (2.41–2.81)	2.58±0.16 (2.32–2.80)	75±8 (60–92)	19.0±8.7 (8–34)	42.0±8.1 (31–63)
August 2005	Wet	4,145±1,038 (2,970–6,140)	1,090±273 (782–1,616)	340±155 (30–577)	14,490±6,434 (1,402–24,638)	2.47±0.11 (2.16–2.66)	2.58±0.59 (2.23–2.82)	51±13 (16–75)	4.3±2.5 (1.2–10.2)	133±129 (26–453)
Wright Myo										
April 2005	Dry	2,870±684 (1,246–4,217)	755±180 (647–1,010)	414±118 (198–585)	19,624±5,223 (9,813–26,930)	2.25±0.15 (1.98–2.49)	2.32±0.15 (1.98–2.50)	44±5 (38–57)	25.0±5.0 (17–34)	56±29 (18–134)
April 2006	Dry	3,671±796 (2,720–6,004)	990±209 (716–1,580)	284±108 (146–583)	15,683±5,991 (8,059–30,636)	2.54±0.04 (2.41–2.60)	2.70±0.61 (2.52–2.63)	69±11 (42–86)	29.7±0.3 (29.1–30.2)	67±20 (24–109)
August 2005	Wet	3,366±821 (1,500–5,072)	886±216 (395–1,335)	357±113 (168–583)	17,156±6,572 (8,449–26,572)	0.90±0.38 (0.37–2.09)	0.86±0.37 (0.84–2.10)	52±17 (23–94)	8.4±7.32 (0.8–28.8)	219±118 (102–568)
August 2006	Wet	3,686±1,025 (1,930–5,490)	970±270 (508–1,445)	283±75 (147–418)	15,644±4,170 (7,290–23,286)	1.75±0.19 (1.45–2.02)	1.84±0.17 (1.45–2.02)	51±11 (30–72)	14.7±4.5 (7.3–21.0)	263±106 (97–428)

also tend to suppress photosynthesis, consistent with low dissolved O_2 during the wet seasons (Table 1). Zhai et al. (2005) similarly found lowest dissolved O_2 during the Pearl Estuary wet season, which was ascribed to elevated heterotrophy, both in contiguous mangrove sediments and their surrounding waters. The lack of seasonal contrast at Wright Myo implies that the effects of any such processes on CO_2 dynamics are insignificant there.

Figures 2, 3 and 4 show temporal trends in carbon system components, dissolved O_2 saturation, salinity and tidal height at Kalighat and Wright Myo. In all surveys tidal height was correlated positively with dissolved O_2 and negatively with pCO_2, CH_4, TAlk and DIC, notwithstanding the correlations for TAlk and DIC being comparatively weak during the Kalighat wet season (Fig. 2). For most surveys the coincidence of maximal pCO_2 and minimal O_2 only broadly matched light-dark periods of photosynthesis-respiration. Most notably, during the Kalighat dry season the data were around 12 h out of phase, maximal O_2 and minimal pCO_2 occurring just prior to midnight (Fig. 2). Overall, the data are consistent with a dominance of tidal pumping, in which mangrove sediment pore waters depleted in O_2 and enriched in the by-products of organic matter oxidation (CO_2, CH_4 and TAlk), seep into creek waters in response to the cyclic rise and fall in hydrostatic pressure (Ovalle et al. 1990), thereby obscuring quasi-coincident cycles in pCO_2 and O_2 driven by photosynthesis-respiration. We previously observed tidal pumping dominance of the diel cycles of CH_4 and N_2O at Wright Myo (Barnes et al. 2006) and Lara and Dittmar (1999) observed tidal pumping of nutrients in Brazilian mangrove waters. Tidal pumping of DIC is also well established in mangrove creeks (Borges et al. 2003; Kristensen et al. 2008; Zablocki et al. 2011; Maher et al. 2013) and has been shown to dominate resulting pCO_2 distributions and CO_2 emissions to air (Borges et al. 2003; Bouillon et al. 2007c; Koné and Borges 2008). The dominance of tidal pumping in the mangrove CO_2 budget was recently demonstrated unequivocally through correlations of pCO_2 with ^{222}Rn, a natural tracer of dissolved pore water inputs (Santos et al. 2012; Maher et al. 2013). Hydrostatic pressure control of mangrove creek biogeochemical variables is thus now firmly established.

At Kalighat, the inverse relationship between CH_4 and tidal height was partially disrupted by heavy rainfall during the first 4 hours of the wet season survey; dissolved CH_4 was suppressed at low water (Fig. 2). This effect was also observed in an earlier study at Wright Myo and ascribed to the suppression of methanogenesis by O_2 penetration of the sediment in the rain drops and by additional dilution with this freshwater flux (Barnes et al. 2006). This mechanism could also enhance the potential for aerobic respiration, consistent with the higher pCO_2 observed. At Kalighat

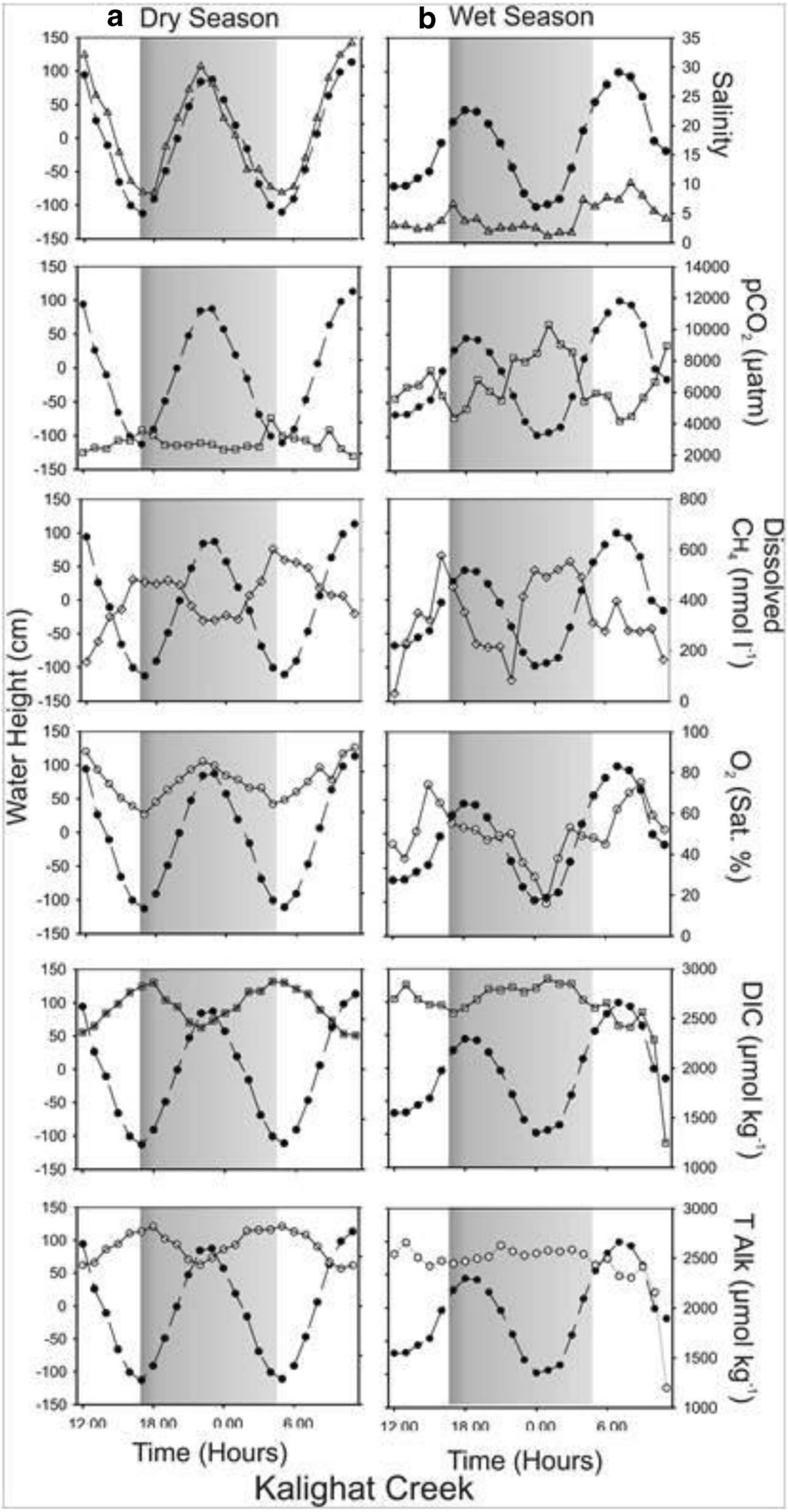

Fig. 2 Tidal variation of water height (*filled circles*), salinity (*open triangles*), pCO$_2$ (*open squares*), dissolved CH$_4$ (*open diamonds*), percent O$_2$ saturation (*open circles*), DIC (*open squares*) and TAlk (*open circles*) at Kalighat Creek during: **a** April 2005 (dry season) and **b** August 2005 (wet season). *Shaded areas* correspond to hours of darkness. Tidal heights are all relative to the mean of the lowest and highest tidal elevations observed during the survey

pCO$_2$ was also higher during nighttime tidal minima than during daytime tidal minima, by ~20 % during the dry season survey and ~14 % during the wet season survey (Fig. 2). Based on this a crude estimate of the maximum photosynthetic removal of the pore water CO$_2$ flux to the overlying creek water is ~20 %.

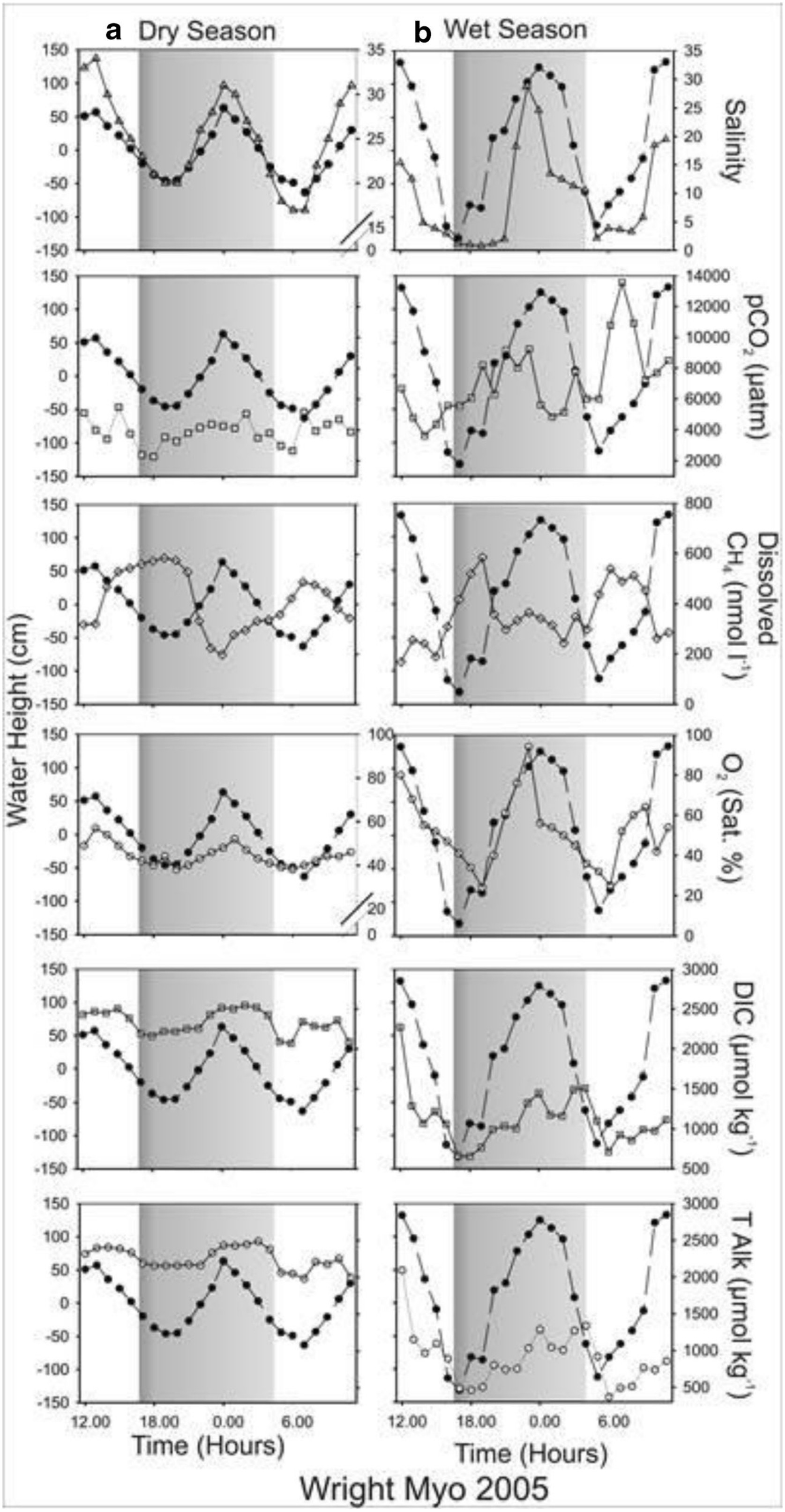

Fig. 3 Tidal variation of water height (*filled circles*), salinity (*open triangles*), pCO$_2$ (*open squares*), dissolved CH$_4$ (*open diamonds*), percent O$_2$ saturation (*open circles*), DIC (*open squares*) and TAlk (*open circles*) at Wright Myo creek during: **a** April 2005 (dry season) and **b** August 2005 (wet season). *Shaded areas* correspond to hours of darkness. Tidal heights are all relative to the mean of the lowest and highest tidal elevations observed during the survey

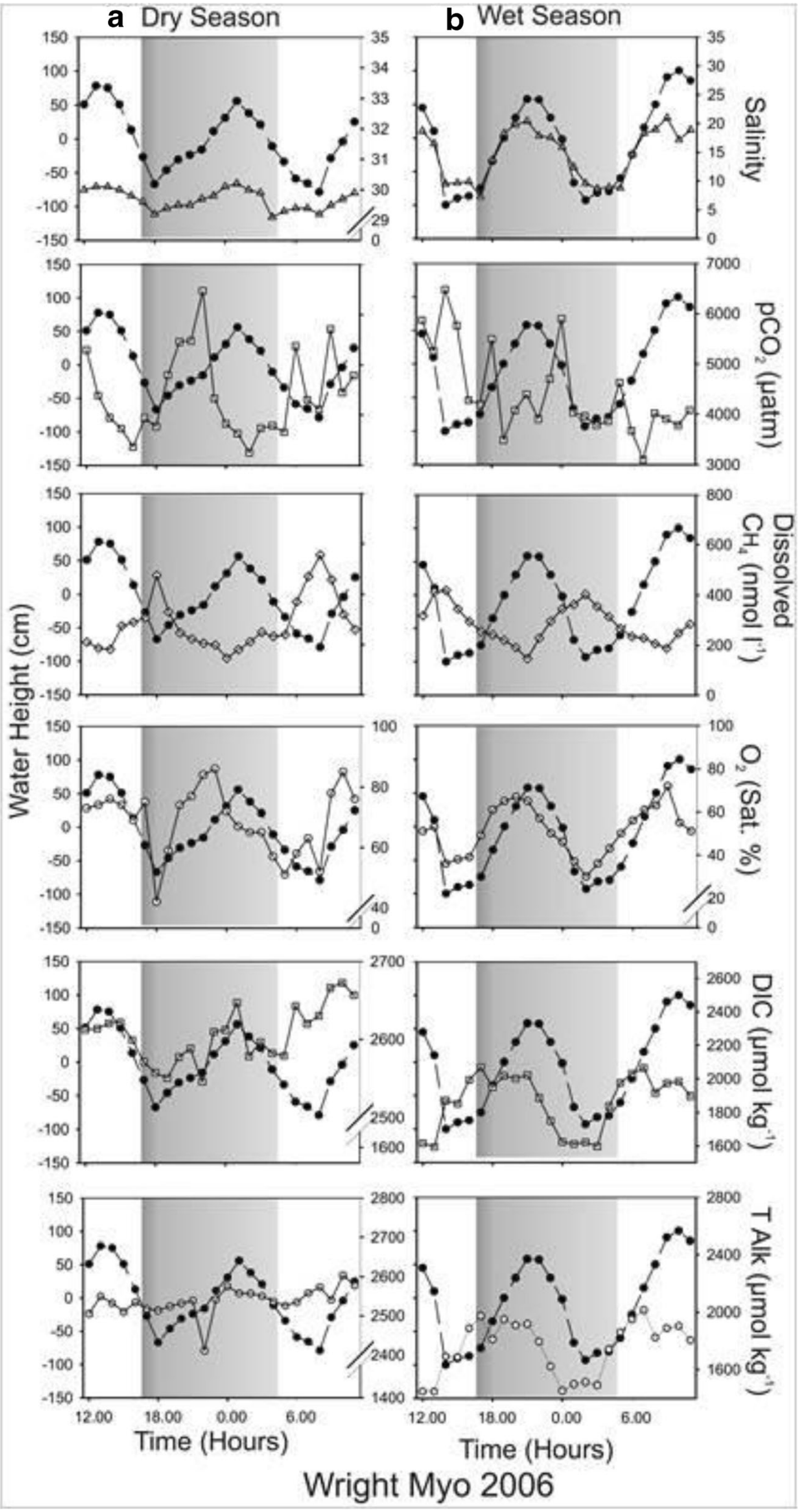

Fig. 4 Tidal variation of water height (*filled circles*), salinity (*open triangles*), pCO$_2$ (*open squares*), dissolved CH$_4$ (*open diamonds*), percent O$_2$ saturation (*open circles*), DIC (*open squares*) and TAlk (*open circles*) at Wright Myo creek during: **a** April 2006 (dry season) and **b** August 2006 (wet season). *Shaded areas* correspond to hours of darkness. Tidal heights are all relative to the mean of the lowest and highest tidal elevations observed during the survey

Porewater production of CO$_2$ and CH$_4$

Net pore water production of CO$_2$ and CH$_4$ reflects several competing diagenetic reactions. Organic matter oxidation via aerobic respiration, denitrification and the reduction of nitrate, sulphate and iron and manganese oxides produces CO$_2$. Methanogenesis can occur via CO$_2$ reduction and from the fermentation of acetate and other low molecular weight compounds that also produces CO_2, and CH_4 is oxidised by sulphate (Berner 1980). Carbonate dissolution and precipitation lead to CO_2 removal and addition respectively, and benthic primary producers are a CO_2 sink (Berner 1980). Despite the complexity, creek water TAlk vs. DIC relationships (Fig. 5) contain important information on the likely dominant diagenetic pathways in creek pore waters. During individual seasons, TAlk and DIC were highly correlated with essentially identical relationships at both sites, but there was a significant seasonal TAlk: DIC offset (wet season, TAlk=0.90 DIC+0.10, r^2=0.99; dry season, TAlk=0.92 DIC+0.20, r^2=0.97; both, n=72). An important detail is that TAlk and DIC concentrations at Wright Myo were lower overall than at Kalighat during both seasons, which could reflect the relative intensities of tidal pumping at the two sites. During the wet season when these differences were greatest (Fig. 5), tidal amplitudes at Kalighat were approximately twice those at Wright Myo (Figs. 2, 3 and 4). An additional possibility is some inter-site variability in organic matter decomposition rates. Alongi et al. (2001) recognise aerobic respiration and sulphate reduction as the major mechanisms of organic matter oxidation in mangrove sediments. However, the first step in organic matter diagenesis is hydrolysis of particulate organic carbon (POC), which yields TAlk but no other DIC (Krumins et al. 2013). While this could account for the observed TAlk intercepts (Fig. 5) and would imply a higher supply rate of reactive POC to mangrove sediments during the dry season (larger TAlk intercept), such an interpretation conflicts with our observations of higher turbidity during the wet season (Table 1), which was interpreted above to reflect higher wet season fluxes of organic carbon, consistent with increased pCO_2 and decreased O_2 deriving from sediment pore waters and a suppression of photosynthesis. Clearly, some remineralisation of POC also could additionally have occurred in the overlying water but our data do not allow any evaluation of this. Interestingly, other work strongly implies such seasonal variability to be insignificant (Bouillon et al. 2007b; Maher et al. 2013). An alternative explanation is that the observed TAlk vs. DIC seasonality (Fig. 5) reflects at least partly, seasonal changes in aerobic respiration and denitrification, the only primary or secondary diagenetic reactions for which ΔDIC exceeds ΔTAlk (Krumins et al. 2013). Higher aerobic respiration during the wet season is consistent with the correspondingly higher pCO_2 and lower O_2 observed (Fig. 2). There is evidence for sediment denitrification at some mangrove sites (Alongi et al 1998, 2000) and a ratio of 0.8 for ΔTAlk/ΔDIC during denitrification (Krumins et al. 2013) is close to that observed in this study (Fig. 5). Even so, denitrification is thought to be a relatively minor contributor to organic matter degradation in most mangrove ecosystems (Alongi et al. 2000; Koné and Borges 2008). Consistent with this, although a substantial pore water source of N_2O in Wright Myo creek waters was previously found, based on concurrent observations of NO_3^- and NO_2^-, this study considered it more likely that this was a consequence of nitrification rather than denitrification (Barnes et al. 2006). Nitrification is a net consumer of TAlk (Krumins et al. 2013) but otherwise leaves DIC unaltered. Iron and manganese reduction have also been found to be important in some Asian mangroves (Alongi et al. 1998; Kristensen et al. 2000) but for both ΔTAlk/ΔDIC is far larger than we observed at Wright Myo or Kalighat. Carbonate dissolution can be a large contributor of TAlk but has a ΔTAlk/ΔDIC ratio of 2 (Krumins et al. 2013). The major diagenetic pathway most consistent with the TAlk and DIC data is sulphate reduction, for which ΔTAlk/ΔDIC is 1 (Krumins et al. 2013). Similar conclusions were reached by Koné and Borges (2008) based on Talk/DIC stoichiometry in waters surrounding Vietnamese mangroves. Having considered all the evidence, it can thus be concluded that the most likely major diagenetic pathway of organic matter oxidation in Andaman mangrove sediments is sulphate reduction, with a variable secondary role for aerobic respiration, broadly in line with previous conclusions for mangroves (Alongi et al. 2001; Koné and Borges 2008).

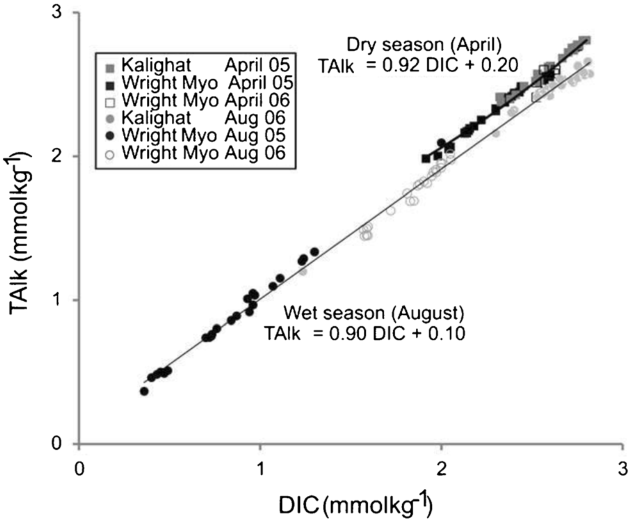

Fig. 5 TAlk vs. DIC during the tidal surveys at Kalighat Creek and Wright Myo

Carbon system components in surface water transects

TAlk vs. salinity or DIC vs. salinity relationships in surface water transects contain information on the potential lateral transport of "tidally pumped" creek waters. TAlk and DIC were linearly correlated in all transects (data not shown). TAlk vs. salinity is shown in Fig. 6. All dry season transects showed a small overall decrease in TAlk with increasing salinity, consistent with a weak but measurable influence of creek water TAlk in even the most offshore samples. By

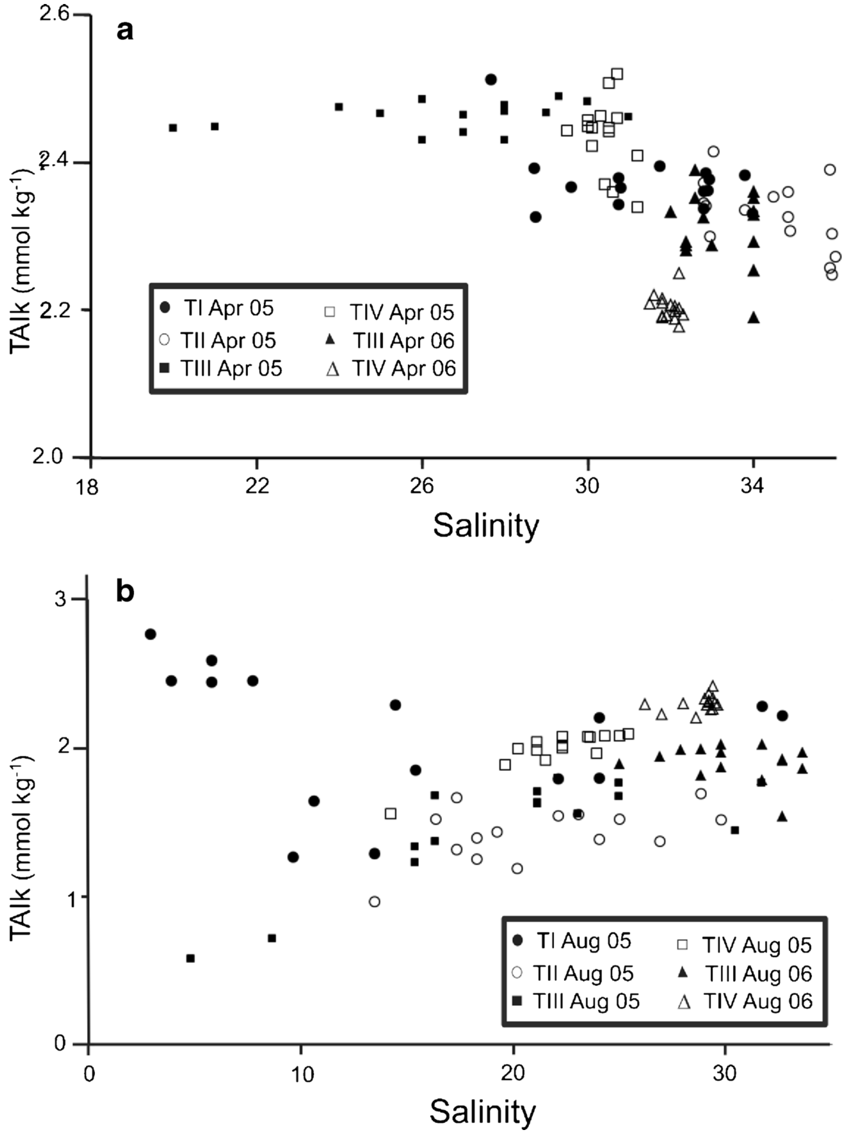

Fig. 6 TAlk vs. salinity during the inshore water transects during: **a** dry (April 2005 and 2006) and **b** wet seasons (August 2005 and 2006)

contrast, the wet season data were much more variable. Although in TI (Kalighat to Mayabander, Aug 2005) an overall decrease in TAlk with salinity was evident, all other wet season transects followed an opposing trend (Fig. 6). Notably, surface (10 m) TAlk concentrations in the Andaman Sea (November) are in the range 2.12–2.16 mmol kg^{-1} (Sarma and Narvikar 2001), essentially identical to much of the wet season data for salinities above 15 (Fig. 6). Evidently, the wet season creek water outflow signal of TAlk was largely masked by these values.

Overall pCO$_2$ and CH$_4$ decreased with salinity in all transects (Fig. 7). Means and ranges of pCO$_2$ were generally highest during the wet seasons whereas means and ranges of CH$_4$ showed no marked seasonality (Table 2). Highest pCO$_2$ and CH$_4$ was observed in TIII (Fig. 7; Table 2), which was in closest proximity to adjacent mangrove creek waters at Wright Myo (Fig. 1). Indeed, seasonality in these transects reflected that at Wright Myo, during 2005 pCO$_2$ was overall lower during the dry season transect than at other times and CH$_4$ showed little temporal variation (Fig. 7; Table 2), consistent with the results of the tidal surveys (Table 1). Whereas CH$_4$ was highly supersaturated at all salinities, CO$_2$ was consistently supersaturated only between Kalighat and Mayabander (TI) and along Wright Myo (TIII), during both the wet and dry seasons (Fig. 7; Table 2). Between Mayabander and Austin Creek (TII), mild CO$_2$ undersaturation at high salinities was observed during April 2005 (dry season), and between Wandoor and Chipiyatapu (TIV), CO$_2$ was always supersaturated only during the August 2006 (wet season) transect. Indeed, TIV had the overall lowest pCO$_2$ and CH$_4$ values of any transect (Table 2), consistent with its being the furthest removed from the influence of mangrove creeks. Undersaturation was observed in one TIV sample during April 2006 but during both the wet and dry

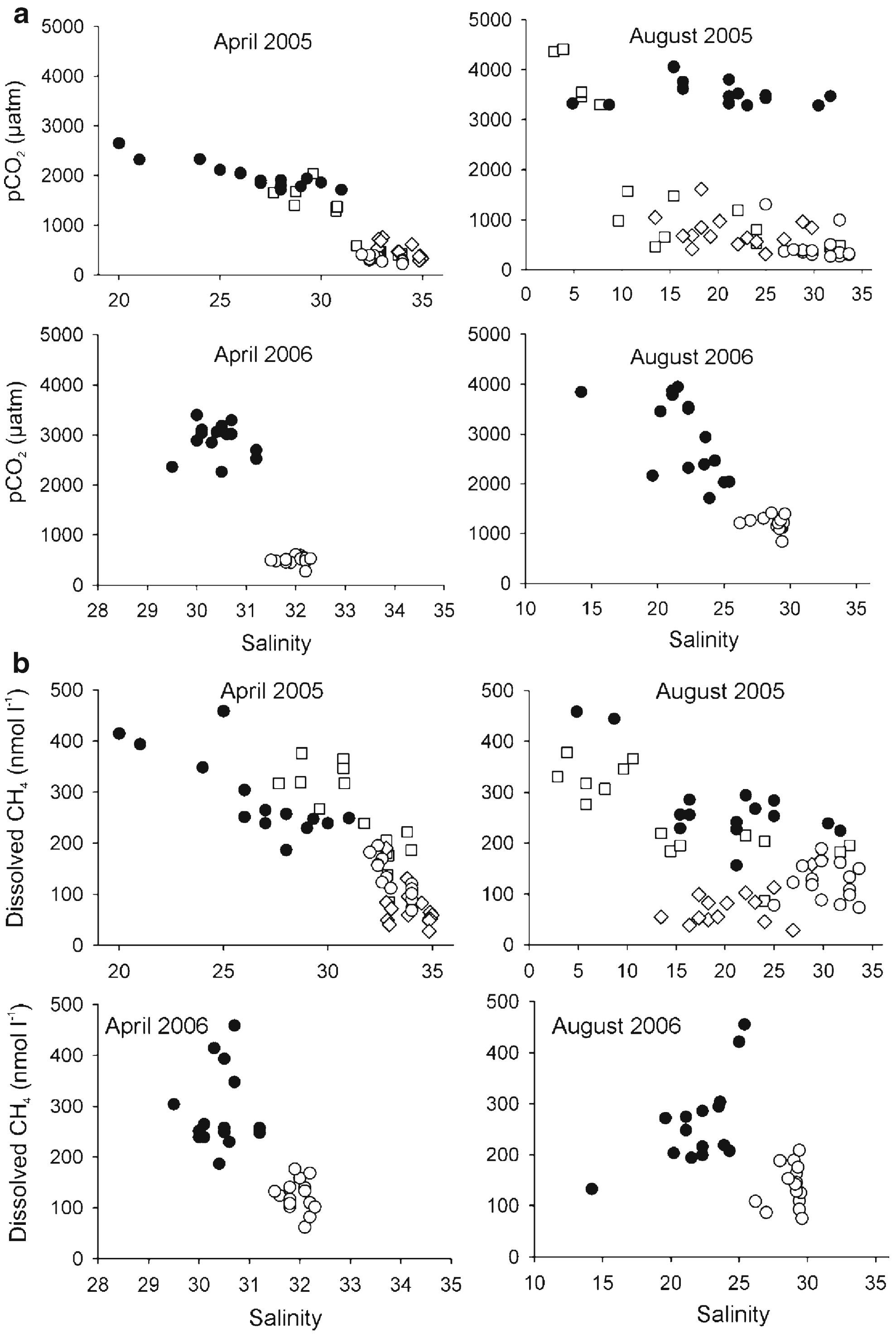

Fig. 7 Variation of **a** pCO$_2$ and **b** dissolved CH$_4$ with salinity in surface water transects: TI (*open squares*), TII (*open diamonds*), TIII (*closed circles*) and TIV (*open circles*). Note the different scales for different seasons

season TIV transects of 2005 CO$_2$ was predominantly undersaturated throughout.

Evidently, creek water tidal pumping can significantly influence the seasonal distributions of pCO$_2$ and CH$_4$ in mangrove-fringing near-shore waters, which like the creeks themselves, are year-round sources of tropospheric CH$_4$. By contrast, the observed distributions of CO$_2$ presumably reflect the balance of net photosynthesis versus creek water inputs. A significant imprint of tidally pumped CO$_2$ and CH$_4$ in mangrove fringing waters is not surprising given that offshore advection of DIC is a likely major export pathway for mangrove carbon (Bouillon et al. 2007c; Maher et al. 2013). Shelf regions are often considered to be net annual CO$_2$ sinks (Chen and Borges 2009). For tropical shelves adjacent to extensive

Table 2 Means and ranges (in brackets) of CO_2, CH_4 and ancillary measurements in inshore water transects

Transect/season	pCO_2 (µatm)	pCO_2 (saturation %)	CH_4 (nmol L^{-1})	CH_4 (saturation %)	TAlk (mmol L^{-1})	DIC (mmol L^{-1})	Temperature (°C)	Salinity
I: Kalighat to Mayabander								
April 2005 Dry	955±592 (381–2,035)	251±156 (100–536)	249±88 (84–376)	11,482±3,970 (3,958–17,024)	2.37±0.04 (2.33–2.51)	2.10±0.11 (1.96–2.27)	29.3±0.4 (28.7–30.5)	31.4±2.0 (29.6–34.0)
August 2005 Wet	1,848±1,508 (454–4,411)	486±396 (119–1,160)	253±84 (86–378)	10,176±3,035 (3,761–14,488)	2.09±0.46 (1.27–2.59)	2.06±0.51 (1.27–2.62)	26.8±0.5 (26.0–27.5)	14.9±9.8 (2.9–32.7)
II: Mayabander to Austin Creek								
April 2005 Dry	486±152 (292–761)	128±40 (77–200)	74±41 (28–190)	3,466±1,897 (1,303–1,897)	2.33±0.05 (2.25–2.42)	2.00±0.05 (1.41–2.10)	28.9±0.9 (25.8–29.4)	24.4±1.3 (32.8–36.0)
August 2005 Wet	762±314 (320–1,613)	201±83 (84–424)	81±42 (28–168)	3,422±1,829 (1,256–7,342)	1.42±0.19 (0.96–1.69)	1.36±0.16 (0.97–1.62)	26.4±0.6 (25.5–27.5)	21.3±4.8 (13.5–29.8)
III: Wright Myo								
April 2005 Dry	1,996±265 (1,710–2,653)	525±70 (450–698)	290±78 (187–459)	12,892±3,240 (8,436–17,608)	2.46±0.02 (2.43–2.49)	2.42±0.03 (2.37–2.47)	28.8±0.4 (27.9–29.3)	26.6±3.1 (20.0–30.0)
August 2005 Wet	3,548±263 (3,285–4,066)	934±69 (864–1,070)	275±79 (157–459)	11,406±2,893 (6,539–17,451)	1.46±0.37 (0.71–1.79)	1.55±0.36 (0.71–1.79)	26.1±0.6 (25.0–27.0)	19.8±7.3 (4.8–31.7)
April 2006 Dry	2,925±329 (2,266–3,398)	770±87 (596–894)	290±78 (187–459)	13,597±3,640 (8,709–21,599)	2.44±0.05 (2.34–2.52)	2.46±0.08 (2.30–2.51)	31.1±0.8 (30.0–32.8)	30.4±0.5 (29.5–31.2)
August 2006 Wet	2,937±802 (1,713–3,948)	773±211 (451–1,039)	262±85 (194–455)	11,480±3,894 (8,435–20,304)	1.99±0.14 (1.55–2.10)	2.05±0.13 (1.66–2.16)	29.1±0.3 (28.2–29.4)	22.0±2.8 (14.2–25.4)
IV: Wandoor to Chipiyatapu								
April 2005 Dry	318±54 (224–412)	84±14 (59–108)	127±39 (68–195)	5,897±1,771 (3,183–9,049)	2.31±0.05 (2.19–2.39)	1.48±0.07 (1.84–2.14)	28.9±0.6 (28.4–30.5)	33.2±0.8 (32.0–34.0)
August 2005 Wet	462±292 (273–1,304)	121±77 (72–343)	124±39 (73–189)	5,476±1,587 (3,340–7,360)	1.90±0.12 (1.54–2.02)	1.68±0.11 (1.47–1.84)	26.4±0.7 (25.5–27.5)	30.4±2.6 (26.9–33.6)
April 2006 Dry	497±76 (277–607)	131±20 (73–160)	124±31 (62–176)	5,832±1,502 (2,905–8,322)	2.20±0.02 (2.18–2.25)	1.90±0.06 (1.67–1.94)	30.5±1.2 (29.4–31.6)	32.0±0.2 (31.5–32.3)
August 2006 Wet	1,199±138 (838–1,415)	316±36 (220–372)	140±41 (75–209)	6,338±1,846 (3,411–9,505)	2.30±0.05 (2.20–2.42)	2.17±0.06 (1.97–2.24)	29.0±0.2 (28.6–29.6)	28.8±1.0 (26.2–29.6)

mangroves with year-round CO_2 export via tidal pumping, this view may require further scrutiny.

Emission fluxes of CO_2 and CH_4

Considering the several potentially important physical and biogeochemical controls of air–sea gas exchange, selecting an appropriate k_w parameterisation is problematic; those in most common use are based on wind speed alone and result in considerable uncertainty (Upstill-Goddard 2006). Two parameterisations specifically applicable in shallow coastal waters where tidal current–seabed interaction generates significant turbulence are Clark et al. (1995) and Borges et al. (2004). Although the latter formally quantifies tidal current velocities and water depth, neither parameterisation has proven universally applicable (Upstill-Goddard 2006). Both were therefore applied to the present data, resulting in an uncertainty range that may be considered typical of such estimates (Upstill-Goddard 2006).

Daily mangrove creek water emissions of CO_2 and CH_4 derived from the Clark et al. (1995) and Borges et al. (2004) relations (Table 3) are the sums of individual hourly estimates over the full 24-h tidal surveys (all, $n=24$). Daily emissions derived from surface transect data (Table 4) are the means of individual daily estimates for each sampling station (all, $n=15$); these emissions were only obtained using Clark et al. (1995) as no water depth or current data are available. Variability in wind speeds was low across all six creek surveys (Table 3); hence the values of k_w derived from Clark et al. (1995) did not vary significantly. Given the almost identical Schmidt numbers of CO_2 and CH_4 (Wanninkhof 1992) k_w derived from Clark et al. (1995) was also essentially identical for both gases in all six surveys: CO_2, 1.31 ± 0.08 cm h^{-1}; CH_4, 1.31 ± 0.07 cm h^{-1} ($n=120$). By contrast, k_w estimates based on Borges et al. (2004) were somewhat more variable: CO_2, 4.08 ± 1.56 cm h^{-1}; CH_4, 4.13 ± 1.63 cm h^{-1}, the difference reflecting changes in water depths and current velocities over tidal cycles. Variations in k_w evidently exert only weak control of Andaman creek CO_2 and CH_4 emissions, which over tidal cycles are primarily functions of changing hydrostatic pressure and porewater concentration gradients. At Kalighat wet season CO_2 emissions derived using Clark et al (1995) were more than twice as high as dry season CO_2 emissions whereas at Wright Myo the seasonal differences were much smaller. By contrast, wet season CO_2 emissions derived using Borges et al (2004) were more than twice as high as dry season emissions at both sites (Table 3). Koné and Borges (2008) reported a similar but larger (fivefold) seasonal trend in CO_2 emissions from Kiên Vàng mangroves in Vietnam, which they attributed to higher net benthic and/or water column heterotrophy during the rainy season, consistent with our earlier explanation for the higher wet season pCO_2 at Kalighat. That the CH_4 data do not support this may be explained by our earlier observation of a significant suppression of mangrove creek CH_4 emissions at Wright Myo immediately following rainfall (Barnes et al. 2006). Consistent with observed simultaneous changes in inorganic nitrogen speciation and turbidity, this behaviour was ascribed to CH_4 oxidation during direct disturbance of the creek sediment surface by raindrops (Barnes et al. 2006). The seasonal variation in Andaman CH_4 emissions was much smaller than for CO_2 overall, irrespective of the k_w formulation used (Table 3). No significant difference between wet and dry season CH_4 emissions at Wright Myo (Barnes et al. 2006) was previously found.

Table 5 summarises previously published emissions of CO_2 and CH_4 from mangrove surrounding waters. In so far as the authors are aware, only three other studies have reported simultaneous such estimates for CO_2 and CH_4 (Ramesh et al. 2007; Bouillon et al. 2007b; Kristensen et al. 2008). Ramesh et al. (2007) summarise our earlier emissions estimates for Wright Myo and Kalighat and it is

Table 3 Emissions fluxes of CO_2 and CH_4 (in millimoles per square meter per day) at Kalighat and Wright Myo

CO_2 emission (mmol m^{-2} day^{-1})					CH_4 emission (mmol m^{-2} day^{-1})	
		Wind speed (m s^{-1})	Clark et al. (1995)	Borges et al. (2004)	Clark et al. (1995)	Borges et al. (2004)
Kalighat						
April 2005	Dry	0.45±0.28	22.7	49.3	0.17	0.38
August 2005	Wet	0.31±0.31	51.9	172.8	0.14	0.47
Wright Myo						
April 2005	Dry	0.40±0.15	30.2	49.3	0.18	0.29
April 2006	Dry	0.20±0.15	37.3	59.5	0.12	0.19
August 2005	Wet	0.29±0.21	39.4	112.3	0.15	0.44
August 2006	Wet	0.17±0.22	38.7	113.8	0.11	0.34
Average of all sites ($n=6$)			36.7±9.8	92.8±49.2	0.15±0.03	0.35±0.10

Table 4 Emissions fluxes of CO_2 and CH_4 (in millimoles per square meter per day) during surface water transects estimated with the Clark et al. (1995) relation

	Transect/season		Wind speed (m s^{-1})	CO_2 emission (mmol m^{-2} d^{-1})	CH_4 emission (mmol m^{-2} day^{-1})
TI	April 2005	Dry	1.45±0.80	7.1	0.14
	August 2005	Wet	2.37±1.72	25.1	0.19
TII	April 2005	Dry	1.18±0.83	1.1	0.04
	August 2005	Wet	2.33±0.95	8.2	0.07
TIII	April 2005	Dry	1.23±0.30	20.7	0.14
	April 2006	Dry	1.04±0.34	24.3	0.14
	August 2005	Wet	0.26±0.16	46.3	0.12
	August 2006	Wet	1.62±1.59	39.2	0.19
IV	April 2005	Dry	2.57±1.03	−1.3	0.10
	April 2006	Dry	2.50±1.90	2.2	0.13
	August 2005	Wet	3.29±1.19	2.6	0.10
	August 2006	Wet	1.10±0.53	10.1	0.07
Average of all transects (*n*=12)				14.7±14.6	0.12±0.05

noteworthy that these are lower than our present estimates, by up to an order of magnitude in the case of CH_4 (Tables 3 and 5). Based on these data, emissions of CO_2 and CH_4 from mangrove creek waters evidently exhibit high inter-annual variability. In other earlier work at Wright Myo we also estimated CH_4 emissions over tidal cycles, in this case using static and floating chambers (Barnes et al. 2006). Our current estimates (Table 3) are at the lower end of this earlier range (Table 5), which is perhaps not surprising given that flux chambers can tend to give larger fluxes than those based on formulations of k_w (Barnes et al. 2006).

The emission estimates for CO_2, both for the tidal creeks and the surface water transects (Tables 3 and 4), appear typical of mangrove associated waters globally (Table 5) whereas the estimated CH_4 emissions (Tables 3 and 4) are towards the low end of the published range (Table 5). However, it should be noted that the CH_4 data in Table 5 span two orders of magnitude because of the inclusion of both anthropogenically impacted and pristine sites. Highest CH_4 emissions, from for example the Jiulonjiang estuary (Alongi et al. 2005) and SE Indian (Purvaja and Ramesh 2001) and Adyar estuary mangroves (Ramesh et al. 2007), tend to reflect urbanisation and/or large inputs of domestic sewage. Kristensen et al. (2008) also found higher CH_4 emissions from an anthropogenically impacted site (Mtoni) than from a pristine site (Ras Dege) in Tanzania although the difference was less pronounced than in these other studies (Table 5). Our new data for Kalightat and Wright Myo (Table 3) support our previous contention that mangrove ecosystems could dominate coastal CH_4 emissions worldwide and that these may have been seriously underestimated in the past (Barnes et al. 2006; Upstill-Goddard et al. 2007), but they do not materially affect previous estimates of mangrove water emissions of either CO_2 or CH_4 globally (Table 5). Worth noting, however, are the observations of substantial ebullition at both Kalighat and Wright Myo during the tidal surveys. These imply that ebullition, which is not quantified in Table 5, may make an important contribution to total emissions, especially for CH_4. This is because bubbles collected at Wright Myo (21 April 2006; dry season) were around 1 % by volume CO_2 (26 times ambient air) and 5 % by volume CH_4 (28000 times ambient air). Studies of CH_4 ebullition in subtropical estuaries (Shalini et al. 2006; Rajkumar et al. 2008), a tropical wetland (Marani and Alvala 2007) and a hypertrophic temperate lake (Casper et al. 2000) estimated ebullition contributions ~60–90 % to total CH_4 emissions. While these results imply that the CH_4 emissions presented in Table 5 could be rather conservative, accurately estimating ebullition fluxes is a substantial challenge (Upstill-Goddard 2006). Consequently, accurately quantifying the ebullition contribution to mangrove water CO_2 and CH_4 emissions requires more detailed study.

Scaling the emission fluxes listed in Table 3 to a creek open water area of~2,700 km^2 gives total Andaman creek water emissions of 3.6×10^{10} mol CO_2year^{-1} and 3.7×10^{7} mol CH_4year^{-1} based on the k_w formulation of Clark et al. (1995). Corresponding emissions derived using the k_w formulation of Borges et al. (2004) are somewhat larger: 9.2×10^{10} mol CO_2year^{-1} and 3.4×10^{8} mol CH_4year^{-1}. Taking an additional account of the contribution from surrounding inshore waters (Table 4) is problematic because the full area extent of the CO_2 and CH_4 outflow plumes is not known, but based on the surveys conducted, these could be estimated to be around ten times the creek area. If so and taking account of their average lower emissions per unit area (around 42 and 71 % respectively, of the creek water values for CO_2 and CH_4; Tables 3 and 4), using k_w derived from Clark et al (1995), the additional emissions could be as much as 1.5×10^{11} mol

Table 5 Previously published estimates of CO_2 and CH_4 emissions from mangrove surrounding waters

Country	Location	CO_2 emission (mmol m^{-2} day^{-1})	CH_4 emission (mmol m^{-2} day^{-1})	Reference
Andaman Islands	Wright Myo		0.43–0.84	Barnes et al. (2006)
Andaman Islands	Wright Myo	65.2	0.01	Ramesh et al. (2007)
Andaman Islands	Kalighat	57.3	0.01	Ramesh et al. (2007)
Australia	Queensland		0.02–0.53	Kreuzwieser et al. (2003)
Bahamas	Normans Pond	13.8±8.3		Borges et al. (2003)
Bermuda	Mangrove Bay	59.8±17.3		Zablocki et al. (2011)
Bermuda	Ferry Reach	5.5±1.3		Zablocki et al. (2011)
Brazil	Itacuracá creek	113.5±104.4		Ovalle et al. (1990)
China	Jiulonjiang Estuary[a]		0–0.1	Alongi et al. (2005)
India	Adyar mangroves[a]	48.7	5.2	Ramesh et al. (2007)
India	Gaderu creek	56.0±100.9		Borges et al. (2003)
India	Godavari Delta	70.2±127.0		Bouillon et al (2003)
India	Moorimgamga creek	23.2±10.1		Ghosh et al. (1987)
India	Muthupet/Cauvery Delta	87.2	0.04	Ramesh et al. (2007)
India	Pichavaram/Cauvery Delta		0.5–1.6	Purvaja et al. (2004)
India	Pichavaram/Cauvery Delta	16.6	0.05	Ramesh et al. (2007)
India	Saptamukhi creek	56.7±37.4		Ghosh et al. (1987)
India	Sundarbans		0.4	Biswas et al. (2004)
India	Sundarbans		0.02–0.14	Biswas et al. (2007)
India	Pichavaram		5.4–20.3	Purvaja and Ramesh (2001)
Kenya	Kidogoweni	71.0±43.0		Bouillon et al (2007b)
Kenya	Kinondo creek	52.0±42.0		Bouillon et al (2007b)
Kenya	Tana river delta	58.0±45.0		Bouillon et al (2007a)
Papua New Guinea	Nagada creek,	43.6±33.2		Borges et al. (2003)
Tanzania	Mtoni[a]	34.5±43.3		Bouillon et al (2008)
Tanzania	Mtoni[a]	3.0–40.0	0.07–0.35	Kristensen et al (2008)
Tanzania	Ras Dege	34.2±27.2		Bouillon et al (2007c)
Tanzania	Ras Dege	1.0–80.0	0.01–0.07	Kristensen et al (2008)
Thailand	Ranong Province		0.20–0.8	Lekphet et al. (2005)
USA	Florida Bay	4.6±5.4		Millero et al. (2001)
USA	Florida mangrove		0.02	Harriss et al (1998)
USA	Shark River, Florida	43.8±52.1		Koné and Borges (2008)
Vietnam	Main channel (dry)[a]	27.1±12.0		Koné and Borges (2008)
Vietnam	Main channel (wet)[a]	81.3±31.8		Koné and Borges (2008)
Vietnam	Kiên Vàng (dry)[a]	32.2±39.4		Koné and Borges (2008)
Vietnam	Kiên Vàng (wet)[a]	154.7±159.1		Koné and Borges (2008)
Vietnam	Tam Giang (dry)[a]	141.5±117.8		Koné and Borges (2008)
Vietnam	Tam Giang (wet)[a]	128.5±110.0		Koné and Borges (2008)

[a] Recognised as significantly anthrogenically impacted by the authors

CO_2 $year^{-1}$ and 2.6×10^8 mol CH_4 $year^{-1}$, giving total emissions of ~1.9×10^{11} mol CO_2 $year^{-1}$ and ~3.0×10^8 mol CH_4 $year^{-1}$ from a total area of mangrove influenced water of ~3×10^4 km^2. Using the k_w formulation of Borges et al. (2004) would undoubtedly yield larger total emissions; however, the lack of water depth and current data for the inshore water transects precludes this.

Mangrove Water Emissions and the Mangrove Carbon Budget

To consider the scale of gaseous carbon emissions from mangrove-associated waters in the context of other compartments of the mangrove carbon budget is instructive. Combining the emissions estimates (Tables 3 and 4) with those compiled in Table 5, an average emissions of ~55±40 mmol $CO_2\,m^{-2}$ day^{-1} and ~1.2±3.0 mmol $CH_4\,m^{-2}$ d^{-1} from mangrove-associated waters can be estimated globally. Our figure for CO_2 is close to an earlier estimate of ~59±52 mmol $CO_2\,m^{-2}$ day^{-1} derived from a slightly smaller dataset (Bouillon et al. 2008). Water column emissions of gaseous carbon are a subset of total sediment emissions and attributing fractional contributions to the total from inundated and exposed sediments individually is problematic because of the intertidal nature of the system. However, a compilation by Bouillon et al (2008) of CO_2 emission estimates derived for exposed mangrove sediments using benthic chambers gave a global average of 61±46 mmol $CO_2\,m^{-2}$ day^{-1}. Given the uncertainties that arise from spatio-temporal variability and measurement methodologies, this is identical to their figure for mangrove waters derived from pCO_2 data, which prompted them to set total global mangrove CO_2 emissions from sediments/water column at ~60±45 mmol m^{-2} day^{-1}, equivalent to ~42±31 Tg C $year^{-1}$. Our estimates for CO_2 and CH_4 do not materially affect this figure considering the inherent uncertainties arising from the high spatio-temporal variability of tidal and inter-tidal mangrove waters and given the above indication that more than 98 % of the total gaseous carbon flux is CO_2.

Additional mangrove carbon sinks include burial and lateral export. Recent work in an Australian mangrove creek provides the first direct estimate of the relative carbon export contributions from DIC, DOC and POC (Maher et al. 2013). This showed DIC export to be at least an order of magnitude greater than DOC export and that POC was consistently imported, at rates comparable to or exceeding, those of DOC export. Given the associated uncertainties the DIC: DOC export ratio is consistent with an earlier synthesis (Bouillon et al. 2008) that set global mangrove carbon sinks (in teragrammes C per year) at: burial, 18.4; DIC export, 178±165; DOC export, 24±21; and POC export, 21±22. Together, these sinks were considered sufficient to balance mangrove net primary production (Bouillon et al. 2008). Clearly, mangrove water emissions of gaseous carbon are a significant term in the mangrove carbon budget, apparently of the same order as DOC and POC fluxes. However, the available data are limited and the associated uncertainties are very large. Importantly, other potentially relevant mechanisms of CO_2 and CH_4 emission remain unaccounted for; for example, crab burrows, which are not routinely included in sediment efflux measurements, may be important conduits for enhanced CO_2 loss (Kristensen et al. 2008), and there is evidence that plant pneumatophores could at least make a significant contribution to total CO_2 emissions (Bouillon et al. 2008) while they may even dominate CH_4 emissions (Purvaja et al. 2004). Moreover, there are no reliable estimates of global mangrove ebullition rates for either CO_2 or CH_4, even though these might well be quantitatively significant.

Conclusions

Our estimates of CO_2 and CH_4 emissions from Andaman mangrove tidal creeks and adjacent inshore waters are within previously published ranges for these systems, consistent with a significant contribution to the mangrove sink for global carbon. Evaluating such emissions in a range of mangrove environments is important to resolving the greenhouse gas balance of mangrove ecosystems globally; however, future such studies should be integral to much wider quantitative process studies of the overall mangrove carbon balance. Improving our current understanding of mangrove carbon dynamics is important, not only for reducing current uncertainties, but for predicting the system response to large-scale changes such as mangrove replanting and clearance, both of which are becoming increasingly important aspects of mangrove "management" and for which the response through gaseous carbon emissions may not be well anticipated.

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