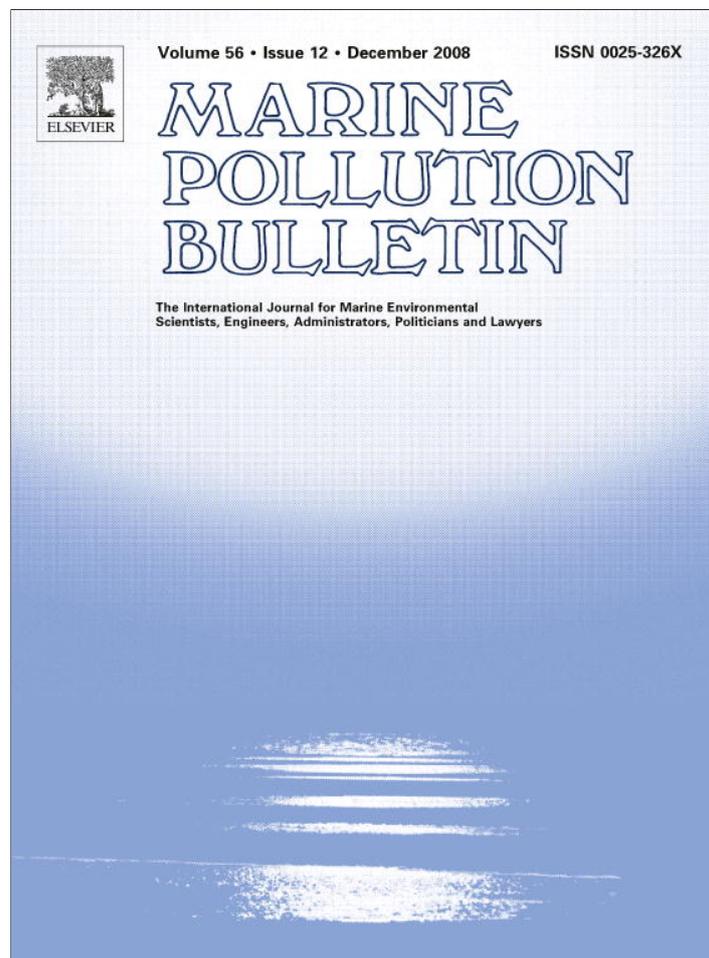


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## Marine Pollution Bulletin

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## Methane and nitrous oxide fluxes in the polluted Adyar River and estuary, SE India

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## ARTICLE INFO

## Keywords:

Tropical and subtropical coasts  
Methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O)  
Nutrients  
Methane ebullition  
Denitrification  
Emissions fluxes

## ABSTRACT

We measured dissolved N<sub>2</sub>O, CH<sub>4</sub>, O<sub>2</sub>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> on 7 transects along the polluted Adyar River–estuary, SE India and estimated N<sub>2</sub>O and CH<sub>4</sub> emissions using a gas exchange relation and a floating chamber. High NO<sub>2</sub><sup>-</sup> implied some nitrification of a large anthropogenic NH<sub>4</sub><sup>+</sup> pool. In the lower catchment CH<sub>4</sub> was maximal ( $6.3 \pm 4.3 \times 10^4$  nM), exceeding the ebullition threshold, whereas strong undersaturation of N<sub>2</sub>O and O<sub>2</sub> implied intense denitrification. Emissions fluxes for the whole Adyar system  $\sim 2.5 \times 10^8$  g CH<sub>4</sub> yr<sup>-1</sup> and  $\sim 2.4 \times 10^6$  g N<sub>2</sub>O yr<sup>-1</sup> estimated with a gas exchange relation and  $\sim 2 \times 10^9$  g CH<sub>4</sub> yr<sup>-1</sup> derived with a floating chamber illustrate the importance of CH<sub>4</sub> ebullition. An equivalent CO<sub>2</sub> flux  $\sim 1\text{--}10 \times 10^{10}$  g yr<sup>-1</sup> derived using global warming potentials is equivalent to total Chennai motor vehicle CO<sub>2</sub> emissions in one month. Studies such as this may inform more effective waste management and future compliance with international emissions agreements.

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## 1. Introduction

Coastal margins in the tropics and subtropics are coming under increasing environmental pressures from enhanced C and N fluxes related to population growth and the intensification of agriculture. Indeed, inverse modelling studies show that the northern hemisphere tropics have been the largest contributor to a global increase in N mobilisation from agriculture and fertilizer production over the past three decades (Hirsch et al., 2006). A significant fraction of this additional anthropogenic C and N is mobilised in surface runoff and subsequently processed microbially in estuaries (Seitzinger and Kroeze, 1998) before its ultimate export to the coastal ocean where it may impact productivity. The degree of estuarine processing is related to the estuarine freshwater residence time. Where freshwater residence times are long the additional organic flux may fuel intense microbial O<sub>2</sub> depletion (Balls et al., 1996) and give rise to important gaseous by-products including CO<sub>2</sub> (e.g. Borges et al., 2004), methane (CH<sub>4</sub>) (e.g. Upstill-Goddard et al., 2000), and nitrous oxide (N<sub>2</sub>O) (e.g. Barnes and Owens, 1999; Barnes, 2003), which consequently are available for sea-to-air-gas transfer. Indeed in such systems atmospheric emission may be the dominant sink so that there may be comparatively little dissolved gas export to adjacent coastal waters (Abril and Borges, 2004).

The atmospheric lifetimes of N<sub>2</sub>O and CH<sub>4</sub> are, respectively,  $\sim 114$  years (Montzka et al., 2003) and  $\sim 8$  years (Lelieveld et al., 1998), and they together account for  $\sim 25\%$  of global mean radiative forcing (Forster et al., 2007). Reaction with tropospheric OH is the

primary atmospheric CH<sub>4</sub> sink (Crutzen, 1995); minor sinks include reaction with free chlorine (Allan et al., 2005) and the formation of stratospheric H<sub>2</sub>O (Crutzen, 1995). Stratospheric N<sub>2</sub>O is the major source of O<sub>3</sub>-depleting NO and NO<sub>2</sub> (Nevison et al., 2004). Variable tropospheric growth rates of N<sub>2</sub>O and CH<sub>4</sub> are related to changing source–sink imbalances but are not well understood (Dlugokencky et al., 1998, 2001; Forster et al., 2007); hence better resolution of their sources and sinks is highly desirable.

The 2007 IPCC assessment sets an open ocean N<sub>2</sub>O source  $\sim 3.8\text{--}5.8$  Tg N yr<sup>-1</sup>, about 10–33% of the global source total of 17.3–17.7 Tg N yr<sup>-1</sup> (Denman et al., 2007). Importantly coastal N<sub>2</sub>O fluxes  $\sim 0.2 \pm 0.14$  Tg N yr<sup>-1</sup> (Nevison et al., 2004), and river and estuarine N<sub>2</sub>O fluxes  $\sim 1.5$  Tg N yr<sup>-1</sup> (Kroeze et al., 2005) are now formally listed by the IPCC as additional anthropogenic sources (Denman et al., 2007), and box model calculations show these to be consistent with the observed rise in atmospheric N<sub>2</sub>O (Kroeze et al., 2005). Some earlier data imply much larger N<sub>2</sub>O fluxes  $\sim 0.3\text{--}6.6$  Tg N yr<sup>-1</sup> from coastal upwelling areas, continental shelves, estuaries, and rivers combined (Bange et al., 1996; Nevison et al., 2004). By contrast marine waters are thought to contribute only a few percent to the total global CH<sub>4</sub> source (Denman et al., 2007). Nevertheless, CH<sub>4</sub> supersaturations  $\sim 21,000\%$  have been observed in some estuaries (e.g. Upstill-Goddard et al., 2000; Abril and Iversen, 2002; Middelburg et al., 2002), hence such regions may be important to local- or regional-scale CH<sub>4</sub> budgets.

The existing coastal emissions estimates for N<sub>2</sub>O and CH<sub>4</sub> are mainly temperate, although more limited tropical data suggest at least similar source functions (e.g. Corredor et al., 1999; Barnes et al., 2006; Upstill-Goddard et al., 2007), thus highlighting a need for additional emissions estimates for these areas. One region

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where such emissions may be especially high is the coastal subcontinent of India. It is well known that Indian rivers deliver some of the highest known particulate C and N loads to the oceans (Ramesh et al., 1995; Gupta et al., 1997; Mukhopadhyay et al., 2002), and these fluxes are likely to increase if current economic growth is sustained. The resulting estuarine cycling of  $N_2O$  and  $CH_4$  may be substantial, especially where anthropogenic inputs are large, but this has yet to be directly assessed.

In this paper, we examine spatial and temporal trends in the concentrations of dissolved  $N_2O$ ,  $CH_4$ , and  $O_2$ , and dissolved inorganic nitrogen (DIN:  $NH_4^+$ ,  $NO_3^-$ ,  $NO_2^-$ ), determined on 7 axial transects from the source of the Adyar River to the mouth of the anthropogenically impacted Adyar estuary, SE India. We also determined  $N_2O$  and  $CH_4$  emissions fluxes directly using flux chambers, and by applying a turbulent-diffusive gas exchange relation to the transect data.

## 2. Methods

### 2.1. Study area

The Adyar River (S.E. India) is ~42 km in length (Fig. 1) and varies in depth from ~0.75 m in its upper reaches to ~0.5 m in its lower reaches. Its source, Chembarambakkam tank, is a natural reservoir. The catchment area is 530 km<sup>2</sup> and the river discharges eastward to the Bay of Bengal via the Adyar estuary (13°0'47"N, 80°16'37"E), which has a mean water depth ~1 m. Annual freshwater discharge is ~1.9–9.4 × 10<sup>8</sup> m<sup>3</sup> (Gowri et al., 2008) but is extremely seasonal; most of the annual precipitation (~1.2 m) occurs during the northeast monsoon (September–December) when freshwater discharge can peak at ~200 m<sup>3</sup> s<sup>-1</sup>, ~7–33 times the annual mean. Additional freshwater sources include surplus water from about 40 small ponds, streams and rainwater drains. The annual temperature range in the Adyar catchment is 18–42 °C. The Adyar is one of two principal rivers passing through the coastal city of Chennai, the fourth largest city in India (metropolitan area ~1200 km<sup>2</sup>, population ~8 million). Central Chennai, the commercial centre which extends ~19 km roughly north–south and ~9 km inland from the Bay of Bengal, is essentially divided in two by the Cooum River, which is of similar size to the Adyar, while the Adyar divides the southern half. Here the Adyar River and estuary are

highly polluted due in large part to extensive, unregulated domestic developments along their banks; discharge of untreated human waste dominates summer flow and may exceed 2 m<sup>3</sup> s<sup>-1</sup> (Ramesh et al., 1997). Sediments in this region have high organic loadings ~3–9% by weight (Purvaja and Ramesh, 2001). Continuous, vigorous “fizzing” of the water surface due to rapid bubble exchange to air is a persistent feature in this region of the Adyar and also further downstream in the estuary, throughout the year (Rajkumar, unpublished data). Total dissolved solids (TDS) typically range from 1 to 20 g l<sup>-1</sup>; values are highest around central Chennai and in the estuary, where a maximum ~30 g l<sup>-1</sup> has been observed (Rajkumar, unpublished data). Between February and August when river flows are low a sand spit becomes established across the mouth of the Adyar estuary due to monsoon-driven long shore drift. This leads to a severe reduction in tidal exchange; the tidal range typically reduces from 0.6 m prior to spit formation to 0.2 m afterward. Consequently the untreated waste and other suspended materials tend to accumulate in the system until the spit is subsequently breached during the NE monsoon floods.

### 2.2. Sampling

Water samples for dissolved  $CH_4$ ,  $N_2O$  and DIN ( $NO_3^-$ ,  $NO_2^-$  and  $NH_4^+$ ) analyses were collected at 0.2 m depth (Richter & Wiese 2.5 dm<sup>3</sup> water sampler) from 20 geographically fixed stations (Fig. 1, Table 1) during 7 axial transects between Chembarambakkam tank and the mouth of the Adyar estuary (Bay of Bengal). Transects were carried out at approximately 2–3 monthly intervals between August 2003 and December 2004; full dates are given in Table 2. Additional samples were collected at station 18 (MRC Nagar) on 05.07.2004 and 14.10.2004. Collection of sub samples (100 cm<sup>3</sup>) for  $CH_4$  and  $N_2O$  analyses followed an established protocol (Upstill-Goddard et al., 1996); samples were inoculated with 0.1 cm<sup>3</sup> HgCl<sub>2</sub> to arrest microbial activity, and dark stored at 4 °C for <12 h during transport to the laboratory. Samples for nutrient analyses were filtered immediately upon collection (Whatman GF/C, 47 mm) and stored in pre-rinsed (0.1 N HCl followed by Milli-RO<sup>®</sup> water; Millipore Corp.; conductivity ~10 μS, bacterial rejection > 99%) HDPE bottles (Nalgene). Filtrates were stored on dry ice during transport to the laboratory (<12 h) and subsequently frozen at -40 °C for a maximum of one week prior to analysis.

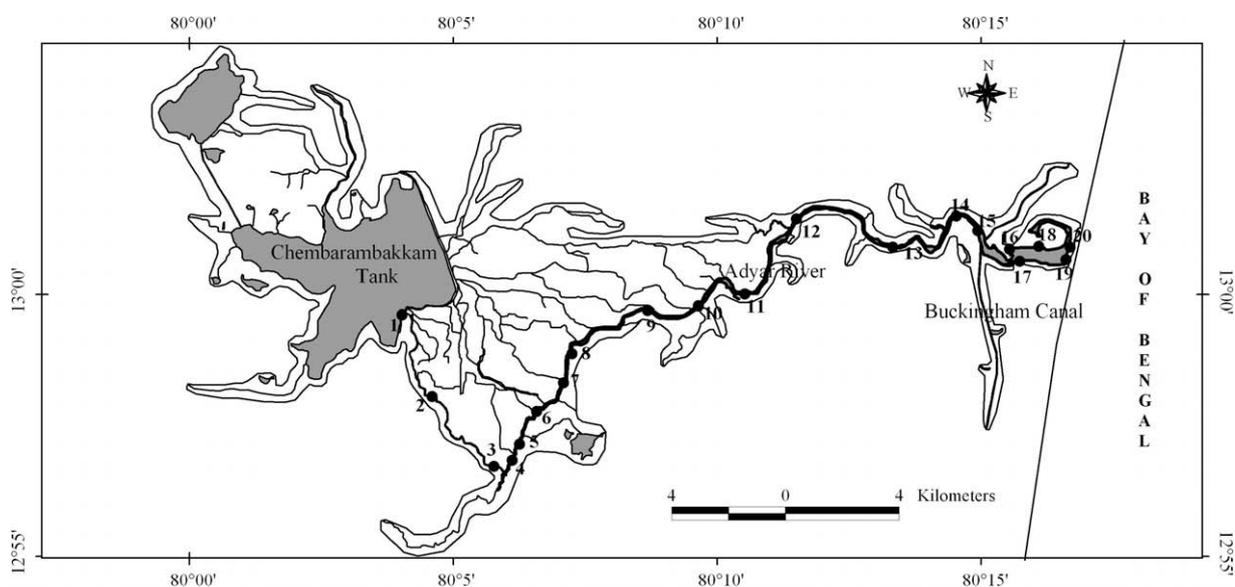


Fig. 1. Sampling sites in the Adyar River and estuary. Numbers indicate distances in kilometres from the source; Chembarambakkam Tank.

**Table 1**  
Details of stations sampled on all 7 axial transects

Station	Location	Coordinates		Mean salinity <sup>a</sup>
<i>Upper catchment</i>				
1	Chembarambakkam Lake	12°56'32.6"N	80°02'14.3"E	0.4 ± 0.4
2	Tiruneermalai	12°57'56.1"N	80°06'49.7"E	0.5 ± 0.4
3	Tiruneermalai Bridge	12°57'16.8"N	80°04'26.8"E	0.5 ± 0.4
4	Anakaputhur Bridge	12°59'10.2"N	80°07'15.6"E	1.1 ± 0.9
5	Polichalur	12°59'39.3"N	80°08'53.8"E	1.0 ± 0.6
6	Korukampakkam	13°00'22.4"N	80°10'00.2"E	1.0 ± 0.6
7	Manapakkam Extn	13°00'22.6"N	80°09'57.6"E	0.7 ± 0.4
8	Nandampakkam	13°01'06.4"N	80°11'05.9"E	1.0 ± 0.7
<i>Lower catchment</i>				
9	Kasi Theatre Bridge	13°01'40.2"N	80°12'31.3"E	0.9 ± 0.6
10	Guindy Industrial Estate	13°01'00.6"N	80°13'00.7"E	0.8 ± 0.3
11	Saidapet Bridge	13°01'04.5"N	80°13'32.0"E	0.9 ± 0.4
12 ±	YMCA	13°01'14.8"N	80°14'09.8"E	1.6 ± 1.6
13	Boat club Avenue	13°01'22.5"N	80°15'14.3"E	1.2 ± 0.8
14	Kotturpuram Bridge	13°01'32.3"N	80°14'32.5"E	1.9 ± 0.5
15	Near Buckingham Canal	80°14'53.5"E	80°14'53.5"E	4.1 ± 3.8
<i>Estuary</i>				
16	Adyar Bridge	13°00'33.8"N	80°15'16.2"E	9.5 ± 11.0
17	Theosophical society	13°00'39.9"N	80°16'32.1"E	8.0 ± 8.7
18	MRC Nagar	13°00'55.9"N	80°16'17.4"E	12.6 ± 10.9
19	Adyar estuary	13°00'59.0"N	80°16'39.8"E	17.8 ± 9.5
20	Bay of Bengal	13°00'59.0"N	80°16'39.8"E	33.7 ± 1.5

<sup>a</sup> Salinities are means ±1 standard deviation of data for each of the 7 axial transects.

We obtained hourly average wind speeds from a meteorological station located at Chennai Airport (12°59'04"N, 80°10'29"E) approximately 7 km south of central Chennai. Data were converted to equivalent wind speeds 10 m above the water surface assuming a logarithmic vertical wind distribution (Mackintosh and Thom, 1973).

### 2.3. Analysis

Dissolved N<sub>2</sub>O and CH<sub>4</sub> were analysed by single-phase equilibration gas chromatography, with electron capture detection (ECD) for N<sub>2</sub>O and flame ionization detection (FID) for CH<sub>4</sub> (Upstill-Goddard et al., 1996). Routine calibration was with a mixed primary standard (9.6 ppmv CH<sub>4</sub>, 1.05 ppmv N<sub>2</sub>O; certified accuracy ± 2%) obtained from the National Physical Laboratory, New Delhi, India (<http://www.nplindia.org/>). Method analytical precision (1σ), determined from repeat analyses (n = 10) of the primary standard, was ±2%. Dissolved gas concentrations were determined using the solubility equations of Wiesenburg and Guinasso (1979) for CH<sub>4</sub> and Weiss and Price (1980) for N<sub>2</sub>O. NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> were analysed by ion chromatography (Metrohm model 761) following the procedure of Michalski (2006). Analytical precision (1σ) was better than ±2%. NH<sub>4</sub><sup>+</sup> was determined by UV spectrophotometry (Hitachi 2000) at 420 nm (Mantoura and Woodward, 1983); analytical precision (1σ) was ±1%. Salinity, temperature and dissolved O<sub>2</sub> were recorded *in situ* using a portable probe (Horiba U-10); precisions (1σ) were ±0.01 salinity, ±0.3 °C, and ±0.01 mg O<sub>2</sub> l<sup>-1</sup>. The dissolved O<sub>2</sub> data were converted to percent saturations using data from Weiss (1970).

### 2.4. CH<sub>4</sub> and N<sub>2</sub>O emissions fluxes

CH<sub>4</sub> and N<sub>2</sub>O emissions fluxes were estimated at all sites using  $F = k_w \Delta C$ , 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>), and  $\Delta C$  is the dissolved gas concentration difference across the air–water interface. For the exchange of sparingly soluble gases their concentrations in air can be ignored, hence  $\Delta C$  is approximated by their concentrations in surface water

(Frost and Upstill-Goddard, 1999). We derived  $k_w$  by appropriate Schmidt number scaling of a  $k_w$ -wind speed relation for CO<sub>2</sub> in estuaries which takes account of turbulence generated both by wind and tidal currents (Clark et al., 1995).

On two additional occasions (05.07.2004 and 14.10.2004) CH<sub>4</sub> and N<sub>2</sub>O emissions fluxes were also measured directly in the Adyar estuary using a free-floating acrylic chamber of 0.2 m<sup>3</sup> internal volume (Barnes et al., 2006). On both occasions the chamber was deployed approximately 2 h prior to high tide from a boat in mid-estuary, at station 18 (MRC Nagar: Fig. 1, Table 1), and allowed to drift for a period of 3 h towards the vicinity of station 16 (Adyar Bridge: Fig. 1, Table 1). Headspace was sampled every 30 min into 12 cm<sup>3</sup> pre-evacuated vials (Isochem; butyl self sealing septum) as in Barnes et al. (2006). Storage was on dry ice as above.

## 3. Results and discussion

For all data spatial variability is the dominant feature of all 7 transects and is independent of salinity (data summarised in Table 1). For ease of presentation data from all transects are shown as functions of downstream distance from Chembarambakkam tank, as whisker plot summaries (Figs. 2–4). For N<sub>2</sub>O and CH<sub>4</sub> these plots are logarithmic because the spatial variability in N<sub>2</sub>O and CH<sub>4</sub> concentrations spans 2 and 3 orders of magnitude, respectively.

In subsequent discussion we refer to three specific regions of the Adyar system, which we have defined according to their overall concentration ranges of dissolved gases and inorganic nutrients: (i) the “upper catchment” (water surface area 1.6 km<sup>2</sup>) defined as the region ~0–14 km downstream from Chembarambakkam tank incorporating stations 1–8 (Fig. 1, Table 1); (ii) the “lower catchment” (water surface area 2.1 km<sup>2</sup>) defined as the polluted region around the centre of the Chennai conurbation region ~14–26 km downstream from Chembarambakkam tank and incorporating stations 9–15 (Fig. 1, Table 1); (iii) the “estuary” (water surface area 3.2 km<sup>2</sup>) defined as the region ~26–40 km downstream from Chembarambakkam tank incorporating stations 16–20 (Fig. 1, Table 1).

### 3.1. Dissolved inorganic nitrogen (DIN) and O<sub>2</sub>

Anthropogenic influence on the N budget of the Adyar system is evidenced by exceptionally high DIN (Table 2). Mean DIN concentrations based on all 7 transects were ~1200 μM in the upper catchment, ~3000 μM in the lower catchment, and ~1200 μM in the estuary (Fig. 2). DIN was always dominated by NH<sub>4</sub><sup>+</sup> regardless of season (range ~625–4300 μM; 95–97% of DIN, Table 2). These NH<sub>4</sub><sup>+</sup> concentrations far exceed those reported for larger Indian systems such as the Hoogly estuary (27–305 μM NH<sub>4</sub><sup>+</sup>; Sadharam et al., 2005), and are higher than those typically found in other rivers considered to be N-rich due to anthropogenic activity (e.g. McMahon and Dennehy, 1999). Even though these high concentrations of NH<sub>4</sub><sup>+</sup> in the Adyar almost certainly are anthropogenic, NH<sub>4</sub><sup>+</sup> dominance of DIN has also been observed at relatively pristine coastal sites in the sub tropics (Barnes et al., 2006), although not to the same extent as in the Adyar. For comparison, concentrations of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> in rivers considered pristine are ~2 μM and ~8 μM, respectively (Meybeck and Ragu, 1997).

In the upper catchment the concentrations of all three DIN components increased with distance downstream (Fig. 2). This region receives significant agricultural runoff, particularly from rice paddies augmented with nitrogenous fertilizers such as urea ((NH<sub>2</sub>)<sub>2</sub>CO) and di-ammonium phosphate ((NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>), which could account for the observed dominance of DIN by NH<sub>4</sub><sup>+</sup>. Nitrification of this NH<sub>4</sub><sup>+</sup>, consistent with high NO<sub>2</sub><sup>-</sup> concentrations ~60 μM in the upper catchment, and ~90 μM in the estuary

**Table 2**  
Mean concentrations of dissolved gases and dissolved inorganic nitrogen (DIN), and some ancillary data, for all 7 axial transects

	Dissolved CH <sub>4</sub> (nM)		Dissolved N <sub>2</sub> O (nM)		Percent O <sub>2</sub> saturation		NH <sub>4</sub> <sup>+</sup> (μM)		NO <sub>3</sub> <sup>-</sup> (μM)		NO <sub>2</sub> <sup>-</sup> (μM)		Rainfall (mm)	Wind speed (m s <sup>-1</sup> )
04th August 2003													126	4.9 ± 2.0
Upper catchment	33	(4–53)	32	(16–61)	104	(79–110)	625	(67–1900)	28	(13–43)	8	(3–16)		
Lower catchment	1860	(9–3240)	44	(4–257)	44	(25–72)	2750	(1800–3300)	8	(2–23)	50	(34–66)		
Estuary	32	(7–41)	19	(7–34)	101	(92–109)	1620	(150–1740)	11	(3–17)	64	(4–82)		
10th October 2003													149	3.3 ± 1.3
Upper catchment	7	(2–32)	9	(7–14)	79	(55–97)	709	(520–1370)	40	(6–76)	20	(2–43)		
Lower catchment	277	(8–950)	16	(7–57)	38	(25–53)	1310	(567–2746)	16	(7–32)	35	(16–85)		
Estuary	47	(5–90)	7	(5–8)	89	(60–121)	720	(522–793)	9	(5–13)	10	(5–14)		
12th December 2003													77	2.4 ± 1.0
Upper catchment	7	(3–10)	9	(6–13)	62	(30–79)	993	(280–2575)	32	(18–46)	19	(5–32)		
Lower catchment	1160	(18–5800)	13	(9–21)	22	(9–49)	4280	(2564–4885)	13	(5–31)	31	(16–52)		
Estuary	30	(10–76)	10	(6–11)	77	(46–111)	1710	(72–2839)	18	(3–46)	97	(9–98)		
27th February 2004													0	3.8 ± 1.2
Upper catchment	2680	(1090–8220)	27	(9–56)	98	(64–111)	1670	(692–2980)	33	(1–71)	50	(22–97)		
Lower catchment	152,000	(14,430–271,000)	7	(6–9)	7	(1–21)	3600	(2236–4035)	42	(13–71)	63	(27–99)		
Estuary	5620	(37–13,700)	44	(6–82)	67	(42–88)	1390	(525–2204)	5	(3–10)	88	(68–98)		
27th May 2004													232	2.7 ± 1.3
Upper catchment	5740	(835–33,170)	29	(6–127)	87	(49–114)	1140	(301–1990)	20	(5–46)	60	(19–98)		
Lower catchment	153,000	(7675–386,000)	8	(7–14)	23	(8–44)	2060	(633–3350)	7	(5–12)	41	(14–68)		
Estuary	3230	(27–6500)	12	(6–13)	35	(11–103)	420	(114–520)	22	(12–31)	26	(10–43)		
19th September 2004													241	3.1 ± 0.7
Upper catchment	7520	(809–14,582)	94	(14–451)	58	(35–82)	1100	(602–2650)	13	(1–36)	15	(1–49)		
Lower catchment	114,000	(4729–202,000)	8	(7–11)	25	(15–40)	3600	(2705–5864)	17	(10–31)	28	(10–45)		
Estuary	2500	(5–3876)	34	(9–46)	83	(47–122)	980	(98–1945)	45	(10–97)	52	(26–62)		
28th December 2004													7	4.8 ± 1.7
Upper catchment	1090	(517–2650)	98	(7–283)	97	(89–104)	2000	(200–5000)	32	(3–72)	68	(32–100)		
Lower catchment	21,600	(16,460–37,550)	6	(4–8)	61	(49–86)	3100	(575–5175)	7	(2–23)	34	(9–78)		
Estuary	4400	(7–12,367)	30	(7–55)	88	(25–130)	890	(50–1775)	9	(3–16)	94	(79–100)		

Numbers in brackets refer to data ranges. Rainfall data are monthly averages immediately prior to sampling and wind speeds are averages for the day of sampling.

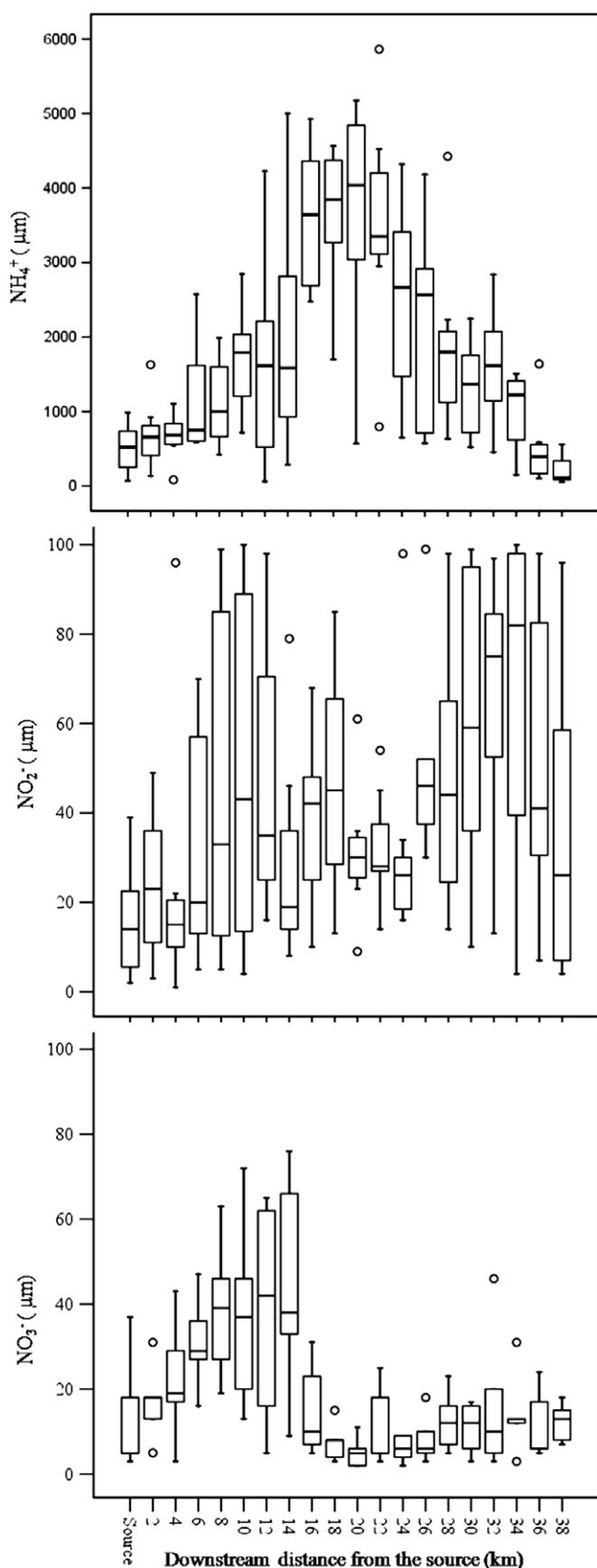
(Table 2, Fig. 2) is the most likely source of the observed concentrations of NO<sub>3</sub><sup>-</sup>; NO<sub>2</sub><sup>-</sup> concentrations > 10 μM generally indicate active nitrification of NH<sub>4</sub><sup>+</sup> (Veeck et al., 2003). Although NH<sub>4</sub><sup>+</sup> concentrations were lower in the Adyar estuary (~720–1630 μM) presumably due to dilution by mixing with seawater, these levels are still very high in comparison to many other estuaries (Barnes, 2003).

Interestingly, whereas NH<sub>4</sub><sup>+</sup> was highest (1300–4300 μM) around the centre of the Chennai conurbation (lower catchment), concentrations of NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> were both relatively low within this zone (Fig. 2), as was dissolved O<sub>2</sub> (Fig. 3). In this region dissolved O<sub>2</sub> saturation was generally below 50% and fell as low as 1% during May 2004 (Table 2, Fig. 3). This and the other exceptionally low dissolved O<sub>2</sub> values observed are due in large part to substantial inhibition of tidal water exchange with the adjacent coastal ocean between February and August when river flows are low. During this period the development of a sand spit across the mouth of the estuary due to monsoon-driven long shore drift typically reduces the tidal range from ~0.6 m to ~0.2 m (Rajkumar, unpublished data). Hence dissolved O<sub>2</sub> in the lower catchment and estuary must be replenished mainly via air–sea gas exchange, which evidently is too slow to keep pace with its biological removal.

### 3.2. CH<sub>4</sub> and N<sub>2</sub>O

Dissolved CH<sub>4</sub> concentrations in the Adyar system span several orders of magnitude both spatially and temporally whereas the range in dissolved N<sub>2</sub>O concentration is much smaller (Table 2, Fig. 4). Broadly the spatial distribution of CH<sub>4</sub> in the Adyar system resembles that of NH<sub>4</sub><sup>+</sup>. In all samples CH<sub>4</sub> was supersaturated with respect to the atmosphere. Concentrations ranged from just above the atmospheric equilibrium value ~2 nM close to Chembarambakkam tank, to ~1.5 × 10<sup>5</sup> nM in the lower catchment (Fig. 4); this is by far the highest CH<sub>4</sub> concentration yet reported

for any natural river–estuarine system. The mean CH<sub>4</sub> concentration in the lower catchment was 6.3 × 10<sup>4</sup> ± 4.3 × 10<sup>4</sup> nM (n = 49), more than an order of magnitude higher than those in the upper catchment (2400 ± 2746 nM; n = 56) and in the estuary (2200 ± 2123 nM; n = 35) (Table 2). For comparison, a comprehensive compilation of CH<sub>4</sub> data from 20 rivers worldwide reveals a wide concentration range: 5–1.2 × 10<sup>4</sup> nM (Upstill-Goddard et al., 2000). The higher value may however be considered exceptional as it derives from an extremely organic-rich tributary of the Amazon; CH<sub>4</sub> in the Amazon mainstem is more typically ~180 ± 30 nM (Richey et al., 1988). Upstill-Goddard et al. (2000) found 4–670 nM CH<sub>4</sub> in two large UK estuaries, Biswas et al. (2007) found 11–129 nM CH<sub>4</sub> in the Hooghly–Matla estuarine system, Bay of Bengal, and Ferrón et al. (2007) found 12–88 nM CH<sub>4</sub> in a shallow tidal creek in the Bay of Cádiz, SW Spain. The exceptionally high levels of dissolved CH<sub>4</sub> in the Adyar are consistent with intense methanogenesis fuelled by the high input rate of organic carbon (Purva and Ramesh, 2001), which is largely composed of fresh domestic organic wastes. At the water temperatures recorded during the surveys (~26–32 °C) rates of methanogenesis would have been close to maximal (Dunfield et al., 1993). Although the sediments almost certainly account for the bulk of the methanogenesis (e.g. Klump and Martens, 1989) TDS concentrations ~10–20 g l<sup>-1</sup> in the lower estuary are not uncommon (Rajkumar, unpublished data). Given the low ambient dissolved O<sub>2</sub> concentrations additional methanogenesis inside suspended particles therefore cannot be excluded and may even be significant, as postulated for the turbidity maxima of some temperate estuaries (Upstill-Goddard et al., 2000). The threshold value of 5 × 10<sup>4</sup> nM dissolved CH<sub>4</sub> beyond which bubbles of free CH<sub>4</sub> form in aquatic sediments (Chanton et al., 1989) was frequently exceeded in the lower catchment; hence the vigorous “fizzing” of the water surface we observed during sampling likely reflects large-scale CH<sub>4</sub> ebullition to air.



**Fig. 2.** Spatial distributions of dissolved inorganic nitrogen (DIN) in the Adyar River and estuary. The data are whisker plot summaries of the 7 transects for each of the locations shown in Fig. 1.

In contrast,  $N_2O$  concentrations were considerably lower and followed an opposite trend to those of  $CH_4$ ;  $N_2O$  was lowest ( $15 \pm 18$  nM;  $n = 49$ ) where  $CH_4$  was maximal, in the lower catchment around the centre of Chennai. Indeed, here  $N_2O$  was always undersaturated (Table 2, Fig. 4) coincident with low dissolved water column  $NO_3^-$ ,  $NO_2^-$  and  $O_2$  (mean  $O_2$  saturation  $31.8 \pm 20.2\%$ ) (Fig. 3). Undersaturation of  $N_2O$  has also been observed in nutrient-rich,  $O_2$ -depleted bottom waters of the Childs River, USA, and attributed to its consumption during benthic denitrification (LaMontagne et al., 2003). Our observations of large  $N_2O$  undersaturation coupled with low dissolved  $NO_3^-$ ,  $NO_2^-$  and  $O_2$  and exceptionally high  $CH_4$  concentrations are consistent with intense anoxia in sediment porewaters of the lower catchment, which in addition to very high rates of methanogenesis leads to the consumption of  $N_2O$  as an electron acceptor during intense denitrification. Even though dissolved  $NH_4^+$  in the lower catchment is exceptionally high we nevertheless conclude that significant nitrification there is unlikely given the low  $O_2$  values and because dissolved  $CH_4$  concentrations greatly exceed the threshold value of 1000 nM required for nitrification inhibition in freshwater sediments (Roy and Knowles, 1994; Ren et al., 2000). Although denitrification is frequently cited as the dominant source of atmospheric  $N_2O$  in organic-rich coastal river estuaries this is evidently not the case in the lower Adyar catchment. Here denitrification instead constitutes a strong  $N_2O$  sink. Higher  $N_2O$  was observed both upstream ( $43 \pm 53$  nM;  $n = 56$ ) and downstream ( $22 \pm 12$  nM;  $n = 35$ ) from this region where conditions are much less reducing (Fig. 4) consistent with its production during net nitrification of  $NH_4^+$  and/or nitrification–denitrification coupling. For comparison Clough et al. (2006) found 36 nM  $N_2O$  in a spring-fed temperate river and Ueda and Ogura (1999) found  $153 \pm 102$  nM  $N_2O$  in a Japanese river contaminated by sewage. For 7 UK estuaries Barnes (2003) found a range of 80–590 nM  $N_2O$ . Bange et al. (1996) found 10–19 nM  $N_2O$  in the Gironde estuary and Ferrón et al. (2007) found 14–50 nM  $N_2O$  in the Bay of Cádiz.

In the Adyar estuary  $N_2O$  exhibited a mid estuarine maximum whereas dissolved  $CH_4$  decreased steadily seaward (Fig. 4). Both of these features have previously been observed in temperate estuaries (e.g. Bange et al., 1998; Barnes and Owens, 1999; Upstill-Goddard et al., 2000; Middelburg et al., 2002).

Seasonal variations in dissolved  $N_2O$  and  $CH_4$  were also significant (Table 2). The highest  $CH_4$  concentrations in the lower catchment and estuary were observed in February 2004, the driest (rainfall 0 mm) and one of the warmest months, but concentrations in the lower catchment in particular were also exceptionally high during both May 2004 and September 2004, the two wettest months (Table 2). Higher  $CH_4$  during the summer is not surprising because of increased rates of methanogenesis coupled with the increased residence time of organic wastes resulting from reduced river discharge, and during October–December the formation of a spit across the estuarine mouth. The importance of the sand spit to estuarine  $CH_4$  levels can be illustrated by comparing December 2003 and December 2004 data (Table 2). During December 2003 a sand spit was not observed, consistent with the abnormally low intensity monsoon during that year. In contrast December 2004 was perhaps more typical; a well defined spit formed across the estuary mouth and consequently estuarine  $CH_4$  concentrations were two orders of magnitude higher than in December 2003. Additionally it has been shown that increased storm water drainage can elevate  $CH_4$  concentrations (Lekphet et al., 2005); hence this may contribute to the high  $CH_4$  concentrations observed in the lower catchment during May and September 2004.

The highest mean  $N_2O$  concentration in the lower catchment was observed during August 2003, one of the wetter months. The DIN data are strong evidence for active nitrification throughout

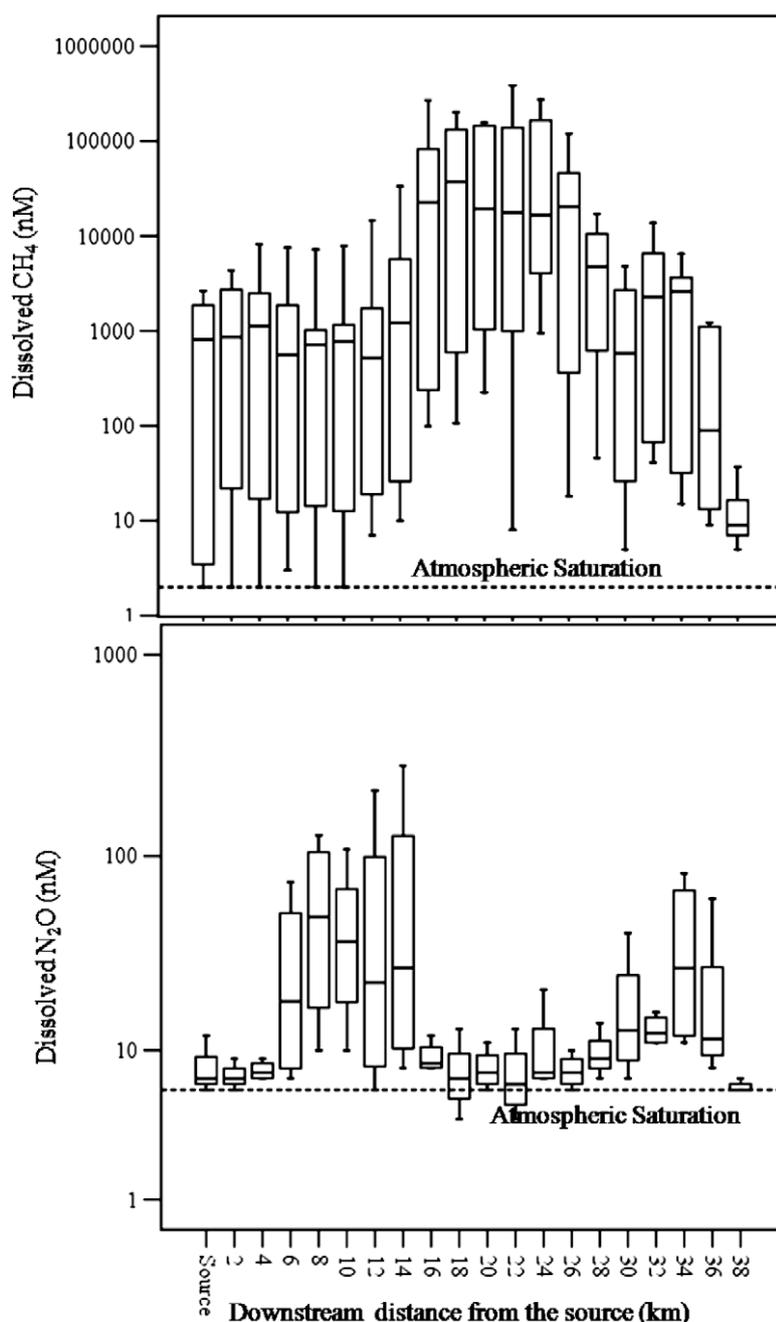


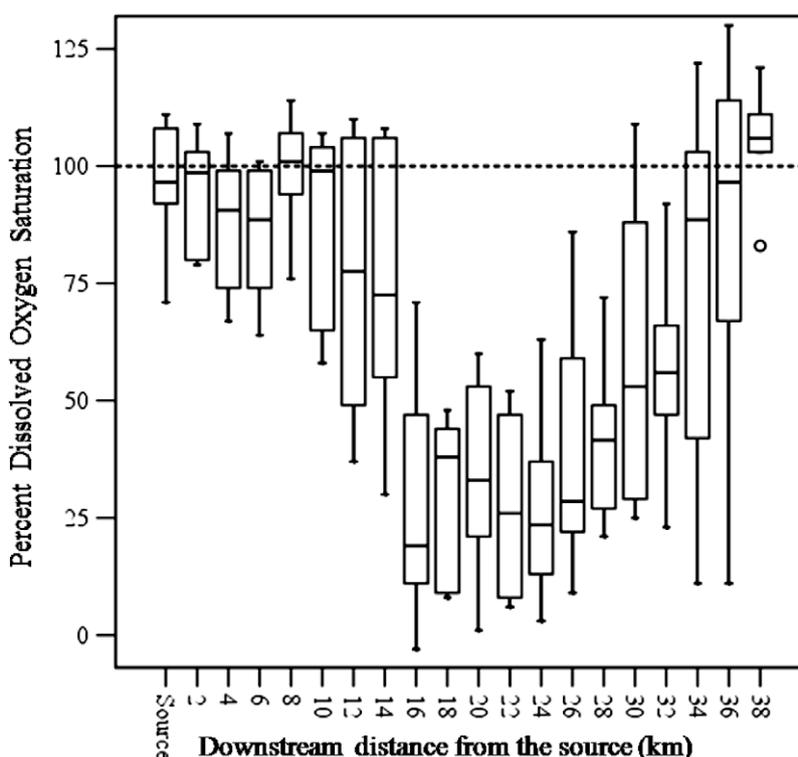
Fig. 3. Spatial distributions of dissolved CH<sub>4</sub> and N<sub>2</sub>O in the Adyar River and estuary. The data are whisker plot summaries of the 7 transects for each of the locations shown in Fig. 1.

the Adyar system (Fig. 2) and a nitrification source for this N<sub>2</sub>O resulting from enhanced mobilisation of soil NH<sub>4</sub><sup>+</sup>, as evidenced by the correspondingly high NO<sub>2</sub><sup>-</sup> (Table 2), can plausibly explain this observation. However, although in the upper catchment the four highest mean N<sub>2</sub>O concentrations coincided with the highest mean NH<sub>4</sub><sup>+</sup> concentrations, this was during both the two wettest months (May and September 2004) and the two driest months (February and December 2004), and the corresponding N<sub>2</sub>O concentrations in the lower catchment were the lowest observed (Table 2). Evidently the relationship between N<sub>2</sub>O (and DIN) and precipitation throughout the catchment is not a simple one. One possibility is that N<sub>2</sub>O production from DIN is related to rain intensity rather than to total rainfall during any given period. A period of low rainfall in the form of intermittent but relatively heavy show-

ers for example might mobilise DIN as efficiently as a more sustained period of lower rain intensity but higher overall rainfall. Coupled with this, variations in freshwater residence times throughout the Adyar system will impact both the extent of N<sub>2</sub>O production via nitrification of NH<sub>4</sub><sup>+</sup>, and in the lower catchment its removal via denitrification.

### 3.3. CH<sub>4</sub> and N<sub>2</sub>O fluxes

Table 3 summarises CH<sub>4</sub> and N<sub>2</sub>O emissions fluxes derived by applying the Clark et al. (1995) relation to the mean wind speeds listed in Table 2, and with the free-floating chamber. Mean annual emissions based on Clark et al. (1995), i.e. excluding the floating chamber estimates, were determined by averaging the individual



**Fig. 4.** Spatial distributions of percent dissolved  $O_2$  saturation in the Adyar River and estuary. The data are whisker plot summaries of the 7 transects for each of the locations shown in Fig. 1.

survey fluxes scaled to one year (Table 3). Summing these, emissions for the whole Adyar system are  $\sim 2.5 \times 10^8$  g  $CH_4$   $yr^{-1}$  and  $\sim 2.4 \times 10^6$  g  $N_2O$   $yr^{-1}$ .

On the two occasions when emissions fluxes were determined by both approaches (05.07.2004 and 14.10.2004)  $N_2O$  fluxes determined with the floating chamber were two and fivefold lower than those derived using the Clark et al. (1995) relation, whereas for  $CH_4$  the floating chamber derived fluxes were both a factor  $\sim 50$  higher. During previous work in a tropical mangrove creek we measured floating chamber fluxes that were on average about 3 times higher than those estimated with the Clark et al. (1995) relation for both  $CH_4$  and  $N_2O$  (Barnes et al., 2006). Some studies have reported floating chambers to overestimate gas exchange relative to other methods (e.g. Clark et al., 1995; Raymond and Cole, 2001) while others find much closer agreement at low wind speeds (e.g. Kremer et al., 2003). Wind speeds during the floating chamber deployments were low:  $3.6 \pm 1.0$  m  $s^{-1}$  (05.07.2004) and  $3.2 \pm 0.9$  m  $s^{-1}$  (14.10.2004), similar to those during the axial surveys (Table 2). While the discrepancies between our floating chamber and turbulent diffusive estimates likely include contributions due to partial shielding of chamber waters from wind and/or wave driven turbulence, the generation of additional water turbulence by the chamber itself, and other methodological differences (e.g. Frost and Upstill-Goddard, 1999), these cannot account for the very large mismatch in our chamber and diffusive  $CH_4$  fluxes given the correspondingly small difference for  $N_2O$  (Table 3). Based on our observations of continuous ebullition and given that dissolved  $CH_4$  frequently exceeded the  $5 \times 10^4$  nM threshold for formation of free sediment  $CH_4$  (Chanton et al., 1989) we must conclude that our chamber fluxes were dominated by  $CH_4$  ebullition, which is not taken account of by gas exchange models based solely on dissolved gas distributions. In support of this we found that changes in  $CH_4$  headspace partial pressures in the floating chambers were not linear with time, in contrast to the situation for  $N_2O$ .  $CH_4$  ebullition

has been shown to greatly exceed diffusive  $CH_4$  fluxes from mangroves (Barnes et al., 2006) and tropical coastal lagoons (Shalini et al., 2006) at low wind speeds, and from a subtropical lake at high wind speeds (Ostrovsky, 2003). "Scavenging" of other gases may also occur during ebullition, by diffusion across the bubble surface (Leifer and Patro, 2002). While this has been demonstrated for several sulphur gases (Roden and Tuttle, 1992; Chanton and Whiting, 1995) there are however no data for  $N_2O$  and our own results provide no supportive evidence for  $N_2O$  scavenging.

Our data (Table 3) indicate that ebullition might account for as much as 97% of the total tropospheric  $CH_4$  flux from the Adyar estuary, although additional measurements are clearly required for verification. Using these very limited flux chamber data to estimate the flux of tropospheric  $CH_4$  from the whole Adyar system thus requires extreme caution, especially given that no chamber flux measurements were made in either the upper or lower catchments. However, given the high organic loading of the lower catchment, its exceptionally high dissolved  $CH_4$  concentrations and its vigorous ebullition, higher chamber  $CH_4$  fluxes there than in the estuary might reasonably be expected. Indeed, the  $CH_4$  emissions from the lower estuary during February, May and October 2004 that were based on the Clark et al. (1995) relation were of the same order as those determined in the estuary using the floating chamber in July and October. Thus by excluding the upper catchment where active bubbling is less evident and using a total area of 5.3 km<sup>2</sup> (lower catchment + estuary) we derive what we consider to be a conservative ebullition flux for the Adyar  $\sim 2 \times 10^9$  g  $CH_4$   $yr^{-1}$ . It is instructive to consider that this is equivalent to around 20% of the atmospheric  $CH_4$  flux  $\sim 10^{10}$  g estimated for the Southern North Sea based on dissolved  $CH_4$  in a number of large UK estuaries in which ebullition plays only a minor role (Upstill-Goddard et al., 2000). Clearly, even small tropical river-estuaries in receipt of large organic fluxes could be comparatively large emitters of tropospheric  $CH_4$ . By contrast although  $N_2O$  emissions from the Adyar

**Table 3**  
CH<sub>4</sub> and N<sub>2</sub>O emissions from the Adyar River and estuary

	CH <sub>4</sub> emission		N <sub>2</sub> O emission	
	( $\mu\text{mol m}^{-2} \text{h}^{-1}$ )	( $10^6 \text{ g yr}^{-1}$ )	( $\mu\text{mol m}^{-2} \text{h}^{-1}$ )	( $10^6 \text{ g yr}^{-1}$ )
<i>Upper catchment</i>				
August 2003	1.0	0.17	1.37	0.84
October 2003	0.1	0.01	0.14	0.09
December 2003	0.1	0.02	0.32	0.20
February 2004	49	8.24	0.61	0.38
May 2004	23	3.78	0.46	0.28
September 2004	103	17.3	1.14	0.70
December 2004	44	7.45	5.10	3.15
Mean		5.29		0.81
<i>Lower catchment</i>				
August 2003	39.3	8.68	1.31	1.06
October 2003	3.43	0.76	0.23	0.19
December 2003	22.8	5.03	0.26	0.21
February 2004	2462	543	0.01	0.01
May 2004	1186	262	0.08	0.06
September 2004	2372	524	0.06	0.05
December 2004	628	139	0.11	0.09
Mean		212		0.24
<i>Estuary</i>				
August 2003	1.95	0.66	1.46	1.8
October 2003	1.68	0.57	0.26	0.32
December 2003	2.02	0.68	0.68	0.84
February 2004	108	36.3	0.49	0.60
May 2004	105	35.3	0.42	0.52
July 2004	93.0	31.3	1.61	1.97
July 2004 <sup>a</sup>	4760	1601	0.27	0.33
September 2004	88.0	29.6	1.46	1.80
October 2004	59.2	19.9	0.30	0.37
October 2004 <sup>a</sup>	2840	955	0.15	0.19
December 2004	460	155	3.54	4.37
Mean <sup>b</sup>		34.3		1.40

<sup>a</sup> Determined using a floating flux chamber.

<sup>b</sup> Excludes floating chamber estimates.

upper catchment and estuary are comparable to those from some much larger UK estuaries on a per unit area basis, the latter being in the range 0.4–3  $\mu\text{mol m}^{-2} \text{hr}^{-1}$  (Barnes, 2003), because of its comparatively small size and the large denitrification sink in the lower catchment the Adyar is a comparatively small source of tropospheric N<sub>2</sub>O.

#### 3.4. Regional relevance of CH<sub>4</sub> and N<sub>2</sub>O emissions from the Adyar

Using emissions fluxes estimated with the Clark et al. (1995) relation 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> (Forster et al., 2007), the Adyar estuary emits the equivalent of  $\sim 1.1 \times 10^{10} \text{ g CO}_2 \text{ yr}^{-1}$  as CH<sub>4</sub> and N<sub>2</sub>O. Adding our chamber flux estimates for CH<sub>4</sub> this increases to  $\sim 9.8 \times 10^{10} \text{ g CO}_2 \text{ yr}^{-1}$ . It is informative to include this estimate in a local greenhouse gas emissions scenario involving the annual CO<sub>2</sub> release from motor vehicles in the Chennai metropolitan area. According to the Department of Economics and Statistics, Government of Tamil Nadu, the number of motor vehicles registered in the Chennai metropolitan area in 2006 was around 1.9 million (<http://www.tn.gov.in/deptst/Stat.htm>). This includes 1.4 million motorbikes (mostly two-stroke), 0.35 million cars, 0.1 million commercial vehicles and buses, and 0.05 million three-wheeler, motorized rickshaws. Based on CO<sub>2</sub> emissions figures of 1.2 kg km<sup>-1</sup> for trucks and buses and 0.25 kg km<sup>-1</sup> for cars in urban use (Albrecht, 2001), and 0.04 kg km<sup>-1</sup> for two stroke motorcycles and motorized rickshaws (McDonald et al., 2005), and assuming an average daily journey of 10 km per vehicle within central Chennai (area  $\sim 20 \text{ km} \times 10 \text{ km}$ ), annual road vehicle CO<sub>2</sub> emissions in Chennai are  $\sim 10^{12} \text{ g}$ . Annual emissions of CH<sub>4</sub> and

N<sub>2</sub>O from the Adyar may therefore be equivalent to more than one month worth of motor vehicle CO<sub>2</sub> emissions. Considering likely direct CO<sub>2</sub> emissions from the Adyar as well, this is expected to rise substantially. Unfortunately there are no available CO<sub>2</sub> data for the Adyar; however it is nevertheless possible to make a crude estimate of the likely relative CO<sub>2</sub> contribution by comparing global and regional estimates of estuarine CO<sub>2</sub> and CH<sub>4</sub> emissions. Abril and Borges (2004) estimated a global estuarine CO<sub>2</sub> emission  $\sim 100\text{--}200 \times 10^{12} \text{ g yr}^{-1}$  whereas estimates of the global estuarine CH<sub>4</sub> emission are in the range  $0.8\text{--}3.0 \times 10^{12} \text{ g yr}^{-1}$  (Bange et al., 1994; Upstill-Goddard et al., 2000; Middelburg et al., 2002). Directly comparing these estimates is somewhat problematic because simultaneous measurements of CO<sub>2</sub> and CH<sub>4</sub> fluxes are rare; hence the databases from which these two estimates are extrapolated do not exclusively use the same estuaries. Frankignoulle et al. (1998) estimated a total annual CO<sub>2</sub> emission  $\sim 1.1 \times 10^{12} \text{ g yr}^{-1}$  for 9 European estuaries and Upstill-Goddard et al. (2000) estimated an annual CH<sub>4</sub> emission  $\sim 7.9 \times 10^9 \text{ g yr}^{-1}$  from UK estuaries bordering the southern N. Sea. The estuaries used in these two studies also differed, however there are some similarities in areal extent and inputs of nutrients and organic carbon. Notwithstanding their clear limitations both of these comparisons imply that typical annual estuarine CO<sub>2</sub> emissions could be around two orders of magnitude higher than those of CH<sub>4</sub>. Adopting this figure would make the Adyar a major contributor to the total anthropogenic flux of tropospheric greenhouse gases in the Chennai region, quite possibly exceeding motor vehicle emissions by at least an order of magnitude.

Tropical and subtropical coastal margins will likely come under even greater environmental pressures during the coming decades, especially in the developing economies. Studies similar to that described here and extended to include the measurement of CO<sub>2</sub> potentially can help define the scale of the problem and inform more effective organic waste management. This will likely become a necessity in view of emerging national commitments to international emissions agreements such as Kyoto and its successors.

#### References

- Abril, G., Borges, A.V., 2004. Carbon dioxide and methane emissions from estuaries. In: Tremblay, A., Varfalvy, L., Roehm, C., Gameau, M. (Eds.), *Greenhouse Gas Emissions: Fluxes and Processes, Hydroelectric Reservoirs and Natural Environments*, Environmental Science Series. Springer, NY, pp. 187–212.
- Abril, G., Iversen, N., 2002. Methane dynamics in a shallow non-tidal estuary Randers (Randers Fjord, Denmark). *Marine Ecology Progress Series* 230, 171–181.
- Albrecht, J., 2001. Tradable CO<sub>2</sub> permits for cars and trucks. *Journal of Cleaner Production* 9, 179–189.
- Allan, W., Lowe, D.C., Gomez, A.J., Struthers, H., Brailsford, G.W., 2005. Interannual variation of <sup>13</sup>C in tropospheric methane: implications for a possible atomic chlorine sink in the marine boundary layer. *Journal of Geophysical Research* 110, D11306. doi:10.1029/2004JD005650.
- Balls, P.W., Brockie, N., Dobson, J., Johnston, W., 1996. Dissolved oxygen and nitrification in the upper Forth estuary during summer (1982–92), patterns and trends. *Estuarine Coastal and Shelf Science* 42, 117–134.
- Bange, H.W., Bartell, U.H., Rapsomanikis, S., Andreae, M.O., 1994. Methane in the Baltic and North Seas and a reassessment of the marine emissions of methane. *Global Biogeochemical Cycles* 8, 465–480.
- Bange, H.W., Dahlke, S., Ramesh, R., Meyer-Reil, L.A., Rapsomanikis, S., Andreae, M.O., 1998. Seasonal study of methane and nitrous oxide in the coastal waters of the southern Baltic Sea. *Estuarine Coastal and Shelf Science* 47, 807–817.
- Bange, H.W., Rapsomanikis, S., Andreae, M.O., 1996. Nitrous oxide in coastal waters. *Global Biogeochemical Cycles* 10, 197–207.
- Barnes, J., 2003. Nitrous oxide in UK estuaries. Ph.D Thesis, University of Newcastle upon Tyne, pp. 158.
- Barnes, J., Owens, N.J.P., 1999. Denitrification and nitrous oxide concentrations in the Humber estuary, UK, and adjacent coastal zones. *Marine Pollution Bulletin* 37, 247–260.
- Barnes, J., Ramesh, R., Purvaja, R., Nirmal Rajkumar, A., Senthil Kumar, B., Krithika, K., Ravichandran, K., Uher, G., Upstill-Goddard, R., 2006. Tidal dynamics and rainfall control N<sub>2</sub>O and CH<sub>4</sub> emissions from a pristine mangrove creek. *Geophysical Research Letters* 33, L15405. doi:10.1029/2006GL026.
- Borges, A.V., Delille, B., Schiettecatte, L.-S., Gazeau, F., Abril, G., Frankignoulle, M., 2004. Gas transfer velocities of CO<sub>2</sub> in three European estuaries

- (Randers Fjord, Scheldt, and Thames). *Limnology and Oceanography* 49, 1630–1641.
- Biswas, H., Mukhopadhyay, S.K., Sen, S., Jana, T.K., 2007. Spatial and temporal patterns of methane dynamics in the tropical mangrove dominated estuary, NE coast of Bay of Bengal, India. *Journal of Marine Systems* 68, 55–64.
- Chanton, J.P., Martens, C.S., Kelley, C.A., 1989. Gas transport from methane-saturated, tidal freshwater and wetland sediments. *Limnology and Oceanography* 34, 807–819.
- Chanton, J.P., Whiting, G.J., 1995. Trace gas exchange in freshwater and coastal marine environments: ebullition and transport by plants. In: Matson, P.A., Harris, R.C. (Eds.), *Biogenic Trace Gases: Measuring Emissions from Soil and Water*. Blackwell, Cambridge, Massachusetts, pp. 98–125.
- Clark, J.F., Schlosser, P., Simpson, H.J., Stute, M., Wanninkhof, R., Ho, D.T., 1995. Relationship between gas transfer velocities and wind speeds in the tidal Hudson River determined by the dual tracer technique. In: *Air–Water Gas Transfer*. AEON Verlag and Studio, Hanau, Germany, pp. 785–800.
- Clough, T.J., Bertram, J.E., Sherlock, R.R., Leonard, R.L., Nowicki, B.L., 2006. Comparison of measured and EF5-r derived  $N_2O$  fluxes from a spring-fed river. *Global Change Biology* 12, 352–363.
- Corredor, J.E., Howarth, R.W., Twilley, R.R., Morell, J.M., 1999. Nitrogen cycling and anthropogenic impact in the tropical interamerican seas. *Biogeochemistry* 46, 163–178.
- Crutzen, P.J., 1995. Overview of tropospheric chemistry: developments during the past quarter century and a look ahead. *Faraday Discussions* 100, 1–21.
- Denman, K.L., Brasseur, G., Chidthaisong, A., Ciais, P., Cox, P.M., Dickinson, R.E., Hauglustaine, D., Heinze, C., Holland, E., Jacob, D., Lohmann, U., Ramachandran, S., da Silva Dias, P.L., Wofsy, S.C., Zhang, X., 2007. Couplings between changes in the climate system and biogeochemistry. In: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M., Miller, H.L. (Eds.), *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, NY.
- Dlugokencky, E.J., Masarie, K.A., Lang, P.M., Tans, P.P., 1998. Continuing decline in the growth rate of the atmospheric methane burden. *Nature* 393, 447–450.
- Dlugokencky, E.J., Walter, B.P., Masarie, K.A., Lang, P.M., Kasischke, E.S., 2001. Measurements of an anomalous global methane increase during 1998. *Geophysical Research Letters* 28, 499–502.
- Dunfield, P., Knowles, R., Dumont, R., Moore, T.R., 1993. Methane production and consumption in temperate and subarctic peat soils: response to temperature and pH. *Soil Biology and Biochemistry* 25, 321–326.
- Ferrón, S., Ortega, T., Gómez-Parra, A., Forja, J.M., 2007. Seasonal study of dissolved  $CH_4$ ,  $CO_2$  and  $N_2O$  in a shallow tidal system of the bay of Cádiz (SW Spain). *Journal of Marine Systems* 66, 244–257.
- Forster, P., Ramaswamy, V., Artaxo, P., Bernsten, T., Betts, R., Fahey, D.W., Haywood, J., Lean, J., Lowe, D.C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., Van Dorland, R., 2007. Changes in atmospheric constituents and in radiative forcing. In: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M., Miller, H.L. (Eds.), *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, NY.
- Frankignoulle, M., Abril, G., Borges, A., Bourge, I., Canon, C., Delille, B., Limbert, E., Thèate, J.M., 1998. Carbon dioxide emission from European estuaries. *Science* 282, 434–436.
- Frost, T., Upstill-Goddard, R.C., 1999. Air–sea gas exchange into the millennium: progress and uncertainties. *Oceanography and Marine Biology: An Annual Review* 37, 12–45.
- Gowri, V., Ramachandran, S., Ramesh, R., Pramiladevi, I.R.R., Krishnaveni, K., 2008. Application of GIS in the study of mass transport of pollutants by Adyar and Cooum Rivers in Chennai, Tamilnadu. *Environmental Monitoring and Assessment* 138, 41–47.
- Gupta, L.P., Subramanian, V., Ittekkot, V., 1997. Biogeochemistry of particulate organic matter transported by the Godavari River, India. *Biogeochemistry* 38, 103–128.
- Hirsch, A.I., Michalak, A.M., Bruhwiler, L.M., Peters, W., Dlugokencky, E.J., Tans, P.P., 2006. Inverse modeling estimates of the global nitrous oxide surface flux from 1998–2001. *Global Biogeochemical Cycles* 20, GB1008. doi:10.1029/2004GB002443.
- Klump, J.V., Martens, C.S., 1989. The seasonality of nutrient regeneration in an organic-rich coastal sediment: kinetic modeling of changing porewater nutrient and sulfate distributions. *Limnology and Oceanography* 34, 559–577.
- Kremer, J.N., Nixon, S.W., Buckley, B., Roques, P., 2003. Technical note: conditions for using the floating chamber method to estimate air–water gas exchange. *Estuaries* 26, 985–990.
- Kroeze, C., Dumont, E., Seitzinger, S.P., 2005. New estimates of global emissions of  $N_2O$  from rivers and estuaries. *Environmental Science* 2, 159–165.
- LaMontagne, M.G., Duran, R., Valiela, I., 2003. Nitrous oxide sources in coastal aquifers and coupled estuarine receiving waters. *Science of the Total Environment* 309, 139–149.
- Leifer, I., Patro, R.K., 2002. The bubble mechanism for methane transport from the shallow sea bed to the surface. a review and sensitivity study. *Continental Shelf Research* 22, 2409–2428.
- Lekphet, S., Nitisoravut, S., Adsavakulchai, S., 2005. Estimating methane emissions from mangrove area in Ranong Province, Thailand. *Songklanakarin Journal of Science and Technology* 27, 153–163.
- Lelieveld, J., Crutzen, P.J., Dentener, F.J., 1998. Changing concentration, lifetime and climate forcing of atmospheric methane. *Tellus B* 50, 128–150.
- Mackintosh, D.H., Thom, A.S., 1973. *Essentials of Meteorology*. Wykeham, London, p. 240.
- Mantoura, R.F.C., Woodward, E.M.S., 1983. Conservative behaviour of riverine dissolved organic carbon in the Severn Estuary: chemical and geochemical implications. *Geochimica et Cosmochimica Acta* 47, 1293–1309.
- McDonald, J., Menter, J., Armstrong, J., Shah, J., 2005. Evaluation of emissions from Asian 2-stroke motorcycles. SAE Technical Paper 2005-32-0114, SAE International, Warrendale, PA, USA, 7 pp.
- McMahon, P.B., Dennehy, K.F., 1999.  $N_2O$  emissions from a nitrogen enriched river. *Environmental Science and Technology* 33, 21–25.
- Meybeck, M., Ragu, A., 1997. River discharges to the oceans: an assessment of suspended solids, major ions and nutrients. UNEP, Nairobi, 245 pp.
- Michalski, R., 2006. Ion Chromatography as a reference method for determination of inorganic ions in water and wastewater. *Critical Reviews in Analytical Chemistry* 36, 107–127.
- Middelburg, J.J., Nieuwenhuize, J., Iversen, N., Hoegh, N., de Wilde, H., Helder, W., Seifert, R., Christof, O., 2002. Methane distribution in European tidal estuaries. *Biogeochemistry* 59, 95–119.
- Montzka, S.A., Fraser, P.J., Butler, J.H., Connell, P.S., Cunnold, D.M., Daniel, J.S., Derwent, R.G., Lal, S., McCulloch, A., Oram, D.E., Reeves, C.E., Sanhueza, E., Steele, L.P., Velders, G.J.M., Weiss, R.F., Zander, R.J., 2003. Controlled substances and other source gases. In: *Scientific Assessment of Ozone Depletion: 2002, Global Ozone Research and Monitoring Project, Report No. 47*. World Meteorological Organization, Geneva.
- Mukhopadhyay, S.K., Biswas, H., De, T.K., Sen, S., Jana, T.K., 2002. Seasonal effects on the air–water carbon dioxide exchange in the Hooghly estuary, NE coast of Bay of Bengal, India. *Journal of Environmental Monitoring* 4, 549–552.
- Nevison, C.D., Lueker, T.J., Weiss, R.F., 2004. Quantifying the nitrous oxide source from coastal upwelling. *Global Biogeochemical Cycles* 18, GB1018. doi:10.1029/2003GB002110.
- Ostrovsky, I., 2003. Methane bubbles in Lake Kinneret: quantification and temporal and spatial heterogeneity. *Limnology and Oceanography* 48, 1030–1036.
- Purvaja, R., Ramesh, R., 2001. Natural and anthropogenic methane emission from coastal wetlands of South India. *Environmental Management* 27, 547–557.
- Ramesh, R., Purvaja, R., Subramanian, V., 1995. Carbon and phosphorus transport by the major Indian rivers. *Journal of Biogeography* 22, 409–415.
- Ramesh, R., Purvaja, R., Parashar, D.C., Gupta, P.K., Mitra, A.P., 1997. Anthropogenic forcing on methane efflux from polluted wetlands (Adyar River of Madras city, India). *Ambio* 26, 369–374.
- Raymond, P.A., Cole, J.J., 2001. Gas exchange in rivers and estuaries: choosing a gas transfer velocity. *Estuaries* 24, 312–317.
- Ren, Q.Y., Chen, G.J., Yan, W., Guo, T.M., 2000. Interfacial tension of  $(CO_2 + CH_4) + water$  from 298 K to 373 K and pressures up to 30 MPa. *Journal of Chemical Engineering Data* 45, 610–612.
- Richey, J.E., Devol, A.H., Wofsy, S.C., Victoria, R., Ribero, M.N.G., 1988. Biogenic gases and the oxidation and reduction of carbon in Amazon River and floodplain waters. *Limnology and Oceanography* 33, 51–561.
- Roden, E.E., Tuttle, J.H., 1992. Sulfide release from estuarine sediments underlying anoxic bottom water. *Limnology and Oceanography* 37, 725–738.
- Roy, R., Knowles, R., 1994. Effects of methane metabolism on nitrification and nitrous oxide production in polluted freshwater sediment. *Applied Environmental Microbiology* 60, 3307–3314.
- Sadhuram, Y., Sarma, V.V., Ramana Murthy, T.V., Prabhakara Rao, P.B., 2005. Seasonal variability of physico-chemical characteristics of the Haldia channel of Hooghly estuary. *Journal of Earth System Science* 114, 37–49.
- Seitzinger, S.P., Kroeze, C., 1998. Global distribution of nitrous oxide production and  $N$  inputs in freshwater and coastal marine ecosystems. *Global Biogeochemical Cycles* 12, 93–113.
- Shalini, A., Ramesh, R., Purvaja, R., Barnes, J., 2006. Spatial and temporal distribution of methane in an extensive shallow estuary, South India. *Journal of Earth System Science* 115, 451–460.
- Ueda, S., Ogura, N., 1999. Mass balance and nitrogen isotopic determination of sources for  $N_2O$  in a eutrophic river. *Japanese Journal of Limnology* 60, 51–65.
- Upstill-Goddard, R.C., Rees, A.P., Owens, N.J.P., 1996. Simultaneous high-precision measurements of methane and nitrous oxide in water and seawater by single phase equilibration gas chromatography. *Deep-Sea Research* 43, 1669–1682.
- Upstill-Goddard, R.C., Barnes, J., Frost, T., Punshon, S., Owens, N.J.P., 2000. Methane in the Southern North Sea: low salinity inputs, estuarine removal and atmospheric flux. *Global Biogeochemical Cycles* 14, 1205–1217.
- Upstill-Goddard, R.C., Barnes, J., Ramesh, R., 2007. Are mangroves a source or a sink for greenhouse gases? In: Tateda, Y., Upstill-Goddard, R., Goreau, T., Alongi, D., Nose, A., Kristensen, E., Wattayakorn, G. (Eds.), *Greenhouse Gas and Carbon Balances in Mangrove Coastal Ecosystems*. Gendai Tosho, Kanagawa, Japan, 257pp, 127–138.
- Veeck, L., Statham, P.J., Hydes, D.J., Smythe-Wright, D., Boswell, S.M., 2003. Are estuarine systems a significant source of  $N_2O$  to the atmosphere? *Geophysical Research Abstracts* 5, 08893. European Geophysical Society.
- Weiss, R.F., 1970. The solubility of nitrogen, oxygen and argon in water and seawater. *Deep Sea Research* 17, 721–735.
- Weiss, R.F., Price, B.A., 1980. Nitrous oxide solubility in water and seawater. *Marine Chemistry* 8, 347–359.
- Wiesenburg, D.A., Guinasso, N.L., 1979. Equilibrium solubilities of methane, carbon monoxide and hydrogen in water and seawater. *Journal of Chemical Engineering Data* 24, 354–360.