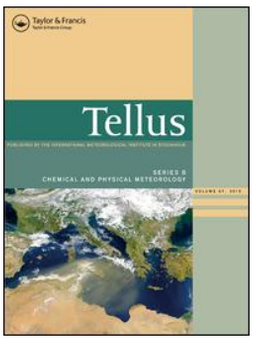

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Contribution of N_2O emissions to the atmosphere from Indian monsoonal estuaries

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ABSTRACT

Estuaries are known to contribute a significant amount of nitrous oxide (N_2O) to the atmosphere; however, the contribution from the Indian estuaries is unknown. We made an attempt to estimate emissions of N_2O from the Indian estuaries by collecting samples from 28 major and minor estuaries along the Indian coast during the wet and dry periods. The N_2O was mostly saturated in all measured Indian estuaries during the study period (72–631%), with exceptionally high saturation in the Ponniyaar estuary (5902%) during the wet period. The N_2O saturation displayed a strong relation with dissolved inorganic nitrogen (DIN; nitrate + nitrite and ammonium), ammonium and dissolved oxygen saturation, suggesting that nitrification is the major source of N_2O in the Indian estuaries. The negative relation between salinity and N_2O saturation suggests inner estuaries are a strong source compared to outer estuaries. The annual mean N_2O saturation ($204 \pm 137\%$) and fluxes (1.3 μmol N_2O m^{-2} d^{-1}) in the Indian estuaries were significantly less than European estuaries (271% and ~2.7 μmol N_2O m^{-2} d^{-1}, respectively). The estimation of flux of N_2O from the European estuaries was also biased due to the inclusion of an exceptionally high supersaturation value from a small UK estuary, Colne (2645%). However, low N_2O saturation and fluxes in the Indian estuaries were related to mean low concentration of DIN that led to low nitrification rates compared to world estuaries. Despite India ranking second in artificial fertilizers use, high flushing rates during the wet period reduce residence time leading to less modification within the estuary.

Keywords: nitrous oxide, fluxes, nitrification, discharge, flushing rate, estuary

To access the supplementary material to this article, please see Supplementary files under Article Tools online.

1. Introduction

Nitrous oxide (N_2O) is an important greenhouse gas, which is 298 times greater with regard to global warming potential (Forster et al., 2007) than carbon dioxide (CO_2), and has a lifetime of 114 year in the atmosphere (IPCC, 2007). Since pre-industrial time atmospheric N_2O has increased ~18% in the atmosphere (IPCC, 2007). Oceans are the second major natural source of N_2O to the atmosphere after soils (Bange et al., 1996; Seitzinger et al., 2000). The N_2O is produced as a by-product in the first step of nitrification and as an obligate intermediate during denitrification. Both nitrification and denitrification occur in water columns, sediments or interior sediment particles (Nevison et al., 2003; Codispoti et al., 2005; Bange, 2008), depending highly on dissolved oxygen concentration (Goreau et al., 1980; De Bie et al., 2002). To the global emission of atmospheric N_2O, aquatic sources contribute ~30% of which 60% come from estuaries and coastal regions (Bange et al., 1996; Seitzinger et al., 2000). Bange (2006) estimated N_2O emission to the atmosphere from European estuaries based on data collected in nine estuaries as $0.33–0.67 \times 10^{12}$ g N annually, which represents up to 26% of global N_2O emission. They further concluded that coastal N_2O is mainly formed in the estuarine system. Recently Barnes and Upstill-Goddard (2011) revised these estimates to $6.8 \pm 13.2 \times 10^9$ g N_2O y^{-1} and noticed that higher estimates by Bange (2006) come from use of a larger area for estuaries.

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Conversely, Bange et al. (1996) estimated N_2O emissions from the world estuaries to be 3.68–5.71 $\times 10^{12}$ g N_2O y^{-1}, and these estimates may have to be revised due to recent modifications in the area of European estuaries. Overall, the estimates from the estuaries suffer from large uncertainties due to large variability and lack of consistent data. It is especially true for Southeast Asian estuaries where the biogeochemical cycling of material is different due to high atmospheric temperature, seasonality of monsoons, and discharge pattern, high fertilizer use, etc. These regions were also highly under-sampled with reference to time and space.

India houses $\sim$220 major and minor estuaries, which are influenced by monsoonal rainfall, and therefore called as monsoonal estuaries. These estuaries have characteristic runoff periods, mostly from June to September when the Indian subcontinent receives rainfall, when they exhibit non-steady state behaviour (Vijith et al., 2009). Seasonal runoff into these monsoonal estuaries far exceeds their total volume and when discharges are at peak level, the entire estuary turns into a river (Sarma et al., 2009, 2010, 2011). Discharges of variable magnitudes occur for a period of 4–6 months, and other periods, the upstream river almost dries up giving place to dominance of seawater in the estuary. Hence, the biogeochemical processes in monsoonal estuaries during discharge period could be completely different from that of a dry period. Recently, Sarma et al. (2012) estimated emissions of CO_2 from the Indian estuaries as $\sim 2 \times 10^{12}$ gC to the atmosphere annually, which is about 10 times less compared to European estuaries. Such low CO_2 fluxes from the Indian estuaries result from high flushing rates and less dense human settlements along the banks of estuaries. In India, N_2O emissions were estimated for the Adayar estuary, in the south east of India, and found to emit $\sim$23.2 μmol N_2O m^{-2} d^{-1} to the atmosphere (Rajkumar et al., 2008). With the exception of this report, no information is available from other Indian estuaries. Indian Mangroves, which are part of the estuarine system, are found to be a strong source of trace gases to the atmosphere (Chauhan et al., 2008; Krithika et al., 2008; Fernandes et al., 2012). The annual emission of N_2O from the mangroves located along the east coast of India was estimated to be 5.8×10^3 gN_2O. The objective of this study is to estimate the contribution of N_2O emissions from the Indian monsoonal estuaries to the atmosphere.

2. Sampling and measurements

In order to examine the variations in N_2O concentrations and related atmospheric fluxes from the Indian estuaries, sampling was conducted in 28 major estuaries along the Indian coast during peak discharge (wet) period (28 July–18th August 2011), and dry period (2–15 January 2012) (Fig. 1). From each estuary, samples were collected at 5–10 locations from river mouth to upper reaches of the estuary. Temperature and salinity were measured using a CTD system (Sea Bird Electronics, SBE 19 plus, USA). Nutrients were measured using a spectrophotometric method following Grashoff et al. (1992). Dissolved oxygen (DO) was measured using Winkler's titration method of Carritt and Carpenter (1966) with a potentiometric end-point detection technique. The analytical precision, expressed as standard deviation, was 0.07% for DO and $\pm$0.2 μM for ammonium, nitrite and nitrate. Dissolved N_2O in the water was determined by a multiphase head space equilibration technique (McAuliffe, 1971) coupled with Gas Chromatographic analysis. Briefly, predetermined volume (25 ml) of sample was equilibrated with an equal volume of helium in a gas tight syringe by vigorously shaking the syringe at room temperature for 5 minutes using a wrist action shaker. After equilibrium, the head space was dried over drierite and then injected through a 5-ml sampling loop into a gas chromatograph (Agilent- 6820, USA) and separated over a chromosorb column (80/100 mesh) at 35°C, and N_2O peak was detected with a ^{63}Ni Electron Capture Detector (ECD). Wind speed data were obtained from the Indian Meteorological Department (IMD) from the stations close to the respective estuaries. The air-to-sea fluxes of N_2O were estimated using the following equation:

$$F(\text{gas}) = K.\ S_{\text{gas}}(\Delta\text{gas})$$

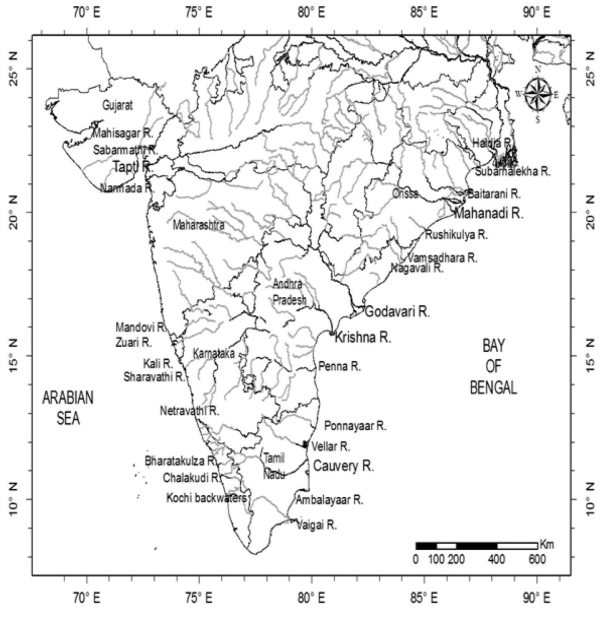

Fig. 1. Station locations map where major rivers are shown with larger font letters. The main course of the river is shown as a dark line while tributaries are shown in grey.

where F (gas) is flux of N_2O (μmol m^{-2} d^{-1}), K is the gas transfer or piston velocity (m d^{-1}; Wanninkhof, 1992), S_{gas} is the solubility coefficient of N_2O (mol m^{-3} atm^{-1}) (Weiss and Price, 1980) and Δgas is the difference between N_2O in water and air (nM).

Hourly measured wind speed was averaged to obtain seasonal mean and was used for piston velocity calculations. The piston velocity at the Schmidt number of 660 (Sc 660) was computed following Wanninkhof (1992):

$$K_{(sc/660)} = 0.31 * u_{10}^2,$$

where Sc is the Schmidt number for N_2O, which was calculated from temperature (t) according to the polynomial fit given and u_{10} is the measured wind speed at the height of 10 m.

Several investigators found that flux estimates based on the Wanninkhof (1992) coefficients may provide underestimates due to the tidal enhancement of turbulence (Zappa et al., 2003; Borges et al., 2004); hence caution is warranted. Nitrification rates were measured using the Schell (1978) method. Briefly, 250 ml of surface sample was incubated in dark for 24 hours by adding 2 μmol of N^{15} labelled ammonium chloride solution (99 atom% excess). After incubation, the nitrate in the water was extracted with aniline and β-napthol, and the resultant Azo-dye was filtered on pre-combusted Whatman GF/F filter. The filter was then dried, packed in the tin cups and combusted in elemental analyser (Flash EA 1112 Series, Thermo Electron, Germany) for content, and the atomic ratio of N^{14}/N^{15} was measured using isotopic ratio mass spectrometer (IRMS; Delta V Plus, Thermo Electron, Germany).

Nitrification rates were measured following uptake rates of substrate (nitrate) enriched with ^{15}N (Dugdale and Goering, 1967). Specific nitrate uptake rates (μmolN l^{-1} d^{-1}) were calculated as:

$$Vn = \left(\left({}^{15}N_p - {}^{15}N_o\right)/\left({}^{15}N_d - {}^{15}N_o\right)T\right) \times N_1,$$

where $^{15}N_p$ is the concentration of ^{15}N (atom%) in the particulate phase after incubation, $^{15}N_o$ is the concentration of ^{15}N (atom%) in the particulate phase at time zero (i.e. natural concentration in the particulate phase), $^{15}N_d$ is the concentration of ^{15}N in the dissolved phase at time zero (i.e. following the ^{15}N enrichment) and T is the incubation time (h). N_1 is the concentration of particulate nitrogen (μmolN l^{-1}).

River discharge data was obtained from dam authorities of respective rivers (Sarma et al., 2012).

3. Results and discussions

The Indian estuaries display a range of hydrological conditions driven by variable freshwater flows and flushing rates during the wet period and variable tidal amplitudes during the dry period. The mean river discharge from the Indian estuaries varied from ~28 to 3505 m^3 s^{-1} (Table 1). The magnitude of discharge determines the amount of organic matter and nutrients entering the estuary and also the stability of water column that governs the interaction with the microbial processes (Sarma et al., 2011, 2012).

The water discharged by the monsoonal estuaries is significantly modified during storage in dam reservoirs. Several dams had been constructed across most rivers sampled in this study. The water is stored in the dam reservoirs for over 6 months during the dry period for irrigation and domestic usage. This storage leads to the formation of stagnant conditions that favour microbial degradation of organic matter and the release of nutrients. Formation of N_2O is possible due to nitrification in the dam reservoir, and discharge of reservoir water into the estuary during the wet period may enhance its concentrations in the estuary. In addition to this, rivers also carry excess fertilizers used in the agricultural farms to the estuary during the wet period. India is ranked second globally in terms of consumption of nitrogen and phosphate as fertilizer (The Fertilizer Association of India, New Delhi) and consumes about 0.025 Tg per year (1 Tg = 10^{12} g). On the other hand, seawater dominates during the dry period due to the closing of dam gates and increased seawater intrusion through tides, resulting in a significant decrease in nutrient levels (Sarma et al., 2010). The relationship between river discharge and DIN indicates that higher DIN concentrations were found in the rivers opened to the east coast compared to the west coast except Narmada, Tapti, Sabarmati and Cochin back waters, which are highly polluted due to local industrial activities (Fig. 2). This relationship is consistent with the fertilizer usage in India, which is higher (~65%) in the regions located along the east coast compared to the west coast (35%) and central India (Ministry of Agriculture, Government of India; http://eands.dacnet.nic.in/latest_2006.html).

3.1. Spatial and temporal variations in N_2O concentrations in the Indian estuaries

The N_2O showed wide variations in the Indian estuaries (Table 1). The concentrations of N_2O (mean ± standard deviation) varied between ~3.5 and 14.6 (6.7 ± 3.5) nM in the estuaries located along the east coast of India while between 6.8 and 47.6 (18.8 ± 11.9) nM in the west coast of India during the wet period. During the dry period, the N_2O concentrations ranged between 4.9 and 22.1 (11.4 ± 5) nM in the estuaries located along the east coast of India, except at the Ponnayar estuary where exceptionally high

Table 1. Annual mean discharge, salinity, oxygen saturation, ammonium, N_2O concentration, saturation, flux and nitrification rates. In the Indian estuaries. Nitrification rates were given only for the dry period

Estuary	Area (km^2)	Annual mean discharge ($m^3\ s^{-1}$)[a]	Salinity[b] (PSU)	Oxygen[b] saturation (%)	NH_4^b (μM)	N_2O[b] (nM)	N_2O[b] Saturation (%)	Flux[b] ($\mu mol\ m^{-2}\ d^{-1}$)	Nitrification rates ($\mu mol\ N\ l^{-1}\ d^{-1}$)
Rivers Flowing towards Bay of Bengal									
Haldia (5) [5]	18.15	1600	4.72 (0.71)	88 (84)	2.4 (1.0)	12.0 (6.9)	148 (105)	0.10 (0.01)	0.092
Subarnalekha (4) [3]	23.15	392	4.31 (3.97)	98 (98)	1.4 (1.4)	8.1 (5.8)	104 (108)	0.01 (0.01)	0.023
Baitarani (3) [9]	22.69	903	18.33 (0.09)	91 (63)	1.5 (3.3)	7.9 (14.0)	108 (229)	0.05 (0.83)	0.131
Rushikulya (3) [11]	12.57	ND	7.35 (20.70)	99 (104)	4.5 (0.3)	4.9 (3.8)	75 (72)	−0.01 (−0.02)	0.047
Mahanadi (3) [16]	13.56	2121	20.41 (0.07)	93 (88)	1.5 (1.7)	7.5 (14.6)	102 (219)	0.01 (0.07)	0.871
Vamsadhara (5) [6]	15.05	ND	12.45 (13.26)	97 (99)	1.7 (1.2)	8.4 (5.3)	122 (97)	0.06 (−0.01)	0.183
Nagavali (2) [3]	13.94	ND	6.43 (28.78)	87 (101)	0.6 (1.4)	19.8 (6.6)	249 (119)	0.41 (0.01)	0.023
Godavari (8) [12]	241.1	3505	21.31 (0.16)	102 (74)	1.8 (1.2)	10.4 (9.5)	162 (156)	0.51 (0.17)	ND
Krishna (3) [12]	36.49	2213	20.55 (5.27)	103 (98)	2.7 (4.9)	7.6 (5.7)	113 (108)	0.02 (0.02)	0.025
Penna (2) [5]	27.97	200	12.11 (9.27)	101 (105)	6.9 (0.6)	19.0 (5.0)	274 (82)	5.36 (−0.10)	0.007
Ponnayaar (2) [5][c]	9.89	ND	7.67 (0.29)	98 (84)	2.3 (2.3)	414 (6.6)	5902 (109)	10.9 (0.01)	0.046
Vellar (2) [5]	20.63	ND	6.92 (11.57)	119 (98)	6.6 (2.0)	8.2 (4.6)	125 (92)	0.05 (−0.08)	ND
Cauvery (3) [7]	20.63	677	5.25 (12.04)	72 (96)	7.6 (0.7)	14.8 (3.5)	221 (86)	0.23 (−0.06)	0.353
Ambalayar (2) [3]	4.57	28	3.86 (4.20)	77 (105)	5.5 (0.8)	8.0 (4.7)	125 (88)	0.18 (−0.04)	ND
Vaigai (3) [6]	0.22	36	12.41 (27.89)	105 (104)	7.9 (0.4)	22.1 (3.5)	327 (78)	3.07 (−1.12)	ND
Rivers flowing towards Arabian Sea									
CB waters (3) [13][c]	231.1	391	8.87 (3.50)	65 (92)	5.2 (3.8)	24.8 (27.7)	385 (391)	3.42 (3.62)	ND
Chalakudi (3) [7]	9.69	ND	14.71 (0.05)	86 (90)	1.6 (2.3)	11.0 (27.1)	180 (392)	0.32 (1.11)	ND
Bharatakulza (2) [6]	19.12	ND	17.56 (0.10)	79 (85)	2.1 (0.8)	10.1 (10)	169 (150)	0.13 (0.19)	ND
Netravathi (2) [7]	18.54	ND	9.94 (0.06)	79 (78)	1.3 (9.1)	14.9 (47.6)	236 (631)	1.76 (7.93)	ND
Kali (2) [6]	17.59	152	9.45 (5.86)	63 (95)	8.0 (5.1)	16.6 (22.5)	240 (329)	0.26 (1.26)	ND
Zuari (3) [15]	14.62	103	20.71 (7.32)	83 (93)	1.8 (16.6)	12.5 (11.5)	195 (187)	12.5 (0.71)	ND
Mandovi (2) [8]	27.68	105	22.84 (0.42)	82 (95)	2.8 (1.4)	9.3 (16.4)	141 (223)	0.43 (1.04)	ND
Narmada (2) [9][c]	115.5	1447	3.82 (0.14)	90 (75)	1.2 (4.0)	26.0 (6.8)	333 (104)	0.14 (0.01)	0.819
Tapti (2) [3][c]	41.04	472	9.33 (0.10)	98 (74)	13.5 (15.3)	42.5 (27.2)	556 (378)	14.21 (12.01)	0.421
Sabarmathi (2) [3][c]	66.29	120	13.51 (0.04)	77 (82)	1.5 (9.7)	16.0 (9.8)	214 (132)	0.07 (0.14)	ND
Mahisagar (2) [3]	14.28	ND	0.23 (0.11)	89 (78)	2.9 (7.2)	47.1 (12.3)	567 (174)	0.29 (0.25)	ND

[a]Discharge data were obtained from Sarma et al. (2012).

[b]Data in the bracket and open represent during the wet and dry periods, respectively. ND denotes no data. Data in square bracket in 1st column represent the number of sampling points in the dry period where as other represent the wet period.

[c]Denotes estuaries which are highly polluted due to local industrial or another anthropogenic activities. CB water represents Cochin Back Waters.

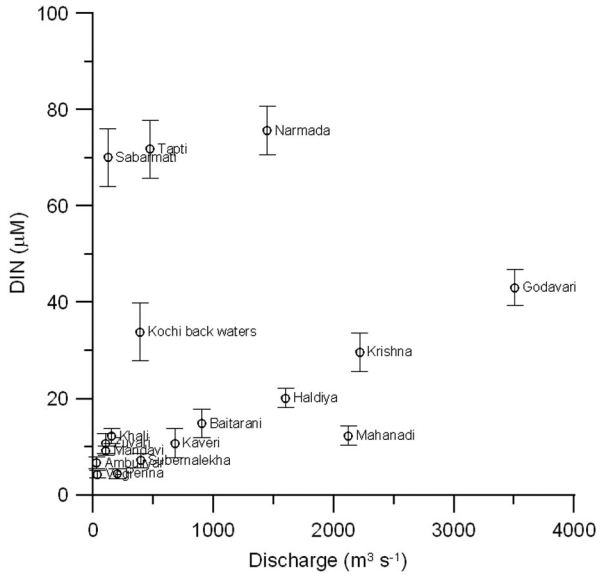

Fig. 2. Relationship between river discharge and dissolved inorganic nitrogen (DIN) during the wet period in the Indian estuaries.

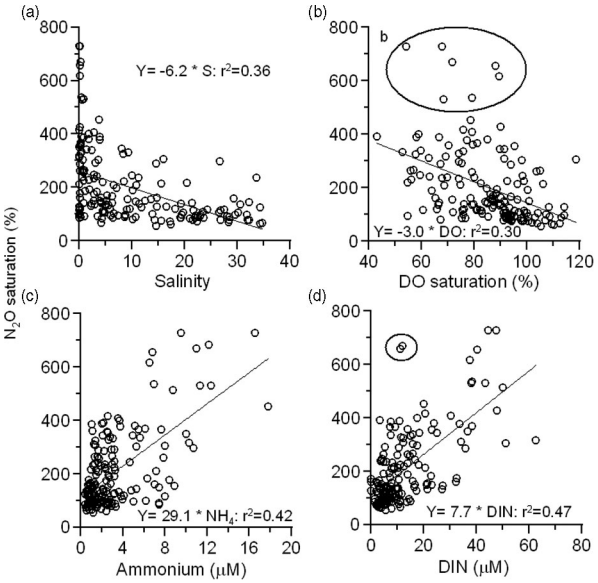

Fig. 3. Relationship of N_2O saturation with (a) salinity, (b) dissolved oxygen saturation (DOsat;%), (c) ammonium concentration (μM) and (d) dissolved inorganic nitrogen (DIN; μM). The points circled in (b) and (d) were excluded in constructing the regression equation, which comes from the polluted estuaries, Narmada and Mahisagar.

N_2O of 414 nM was recorded, and between 9.3 and 47.1 (21.0 ± 13) nM in the west coast of India. The mean concentrations of N_2O were slightly higher during the dry period (15.5 ± 10 nM) than the wet period (12.0 ± 10 nM) in the Indian estuaries. Super-saturation of N_2O was noticed in the Indian estuaries with relatively lower values associated with estuaries located on the east coast ($108 \pm 53\%$) than on the west coast of India ($290 \pm 158\%$) during the wet period. On the other hand, comparatively higher saturation was observed in the estuaries located along the east coast of India ($161 \pm 76\%$) during dry than the wet period and no significant seasonal variations being noticed in estuaries located along the west coast of India ($292 \pm 150\%$).

The N_2O saturation showed weak inverse correlation with salinity ($r^2 = 0.36$; $p < 0.05$) with large scatter, especially at the lower salinity region in the Indian estuaries (Fig. 3a). In order to examine the scatter in the relationship, we have plotted these relationships for selected estuaries from both the east and west coasts of India in Fig. 4. The strong correlation was observed when salinity and N_2O data were plotted for individual estuaries. The slope of the relation was changed among estuaries and ranged between 2.8 and 16.1, whereas it ranged from 3.8 to 15.1 and 47.2 to 188.3 with DO saturation and ammonium, respectively, suggesting that the scatter in the relationship was the result of variations in the slopes. The variable slopes of the relationship suggest that the concentration of N_2O in the freshwater received by the Indian estuaries is different. Though the relation between salinity and N_2O was shown only for a few estuaries in Fig. 4, a similar relationship was found for other estuaries also. Nevertheless, the salinity to N_2O relationship suggests that the estuaries which receive high freshwater inputs from upstream act as a stronger source of N_2O than others (Figs. 3a and 4). An increase in N_2O saturation with a decrease in salinity was reported in several estuaries (Berounsky and Nixson, 1993; Bange, 2006; Silvennoinen et al., 2008; Zhang et al., 2010). Similarly, N_2O saturation showed an inverse relation with dissolved oxygen saturation ($r^2 = 0.30$; $p < 0.05$; Fig. 3b), whereas it showed a positive relation with ammonium ($r^2 = 0.42$; $p < 0.001$; Fig. 3c) and with DIN ($r^2 = 0.47$; $p < 0.001$; Fig. 3d), suggesting that nitrification is the possible mechanism for the production of N_2O in the Indian estuaries. Berounsky and Nixson (1993) observed an increase in nitrification rates with an increase in DIN in Narragansetti Bay, USA. Bange et al. (1996) and Barnes and Upstill-Goddard (2011) suggested that N_2O in the European estuaries was contributed to by nitrification. Relatively higher N_2O saturation in the west coast estuaries was associated with higher DIN concentrations (36 ± 26 μM) than east coast estuaries (15.8 ± 22 μM; Fig. 2). In addition to this, dissolved oxygen saturation was also lower in the west coast estuaries ($83 \pm 8\%$) than east coast estuaries ($94 \pm 6\%$) (Table 1). The east–west gradients in the nutrients load could possibly be due to either overconsumption of fertilizers or intense remineralization of organic matter in the estuary. The state-wise fertilizer consumption in India suggests that ~65% of the fertilizers are

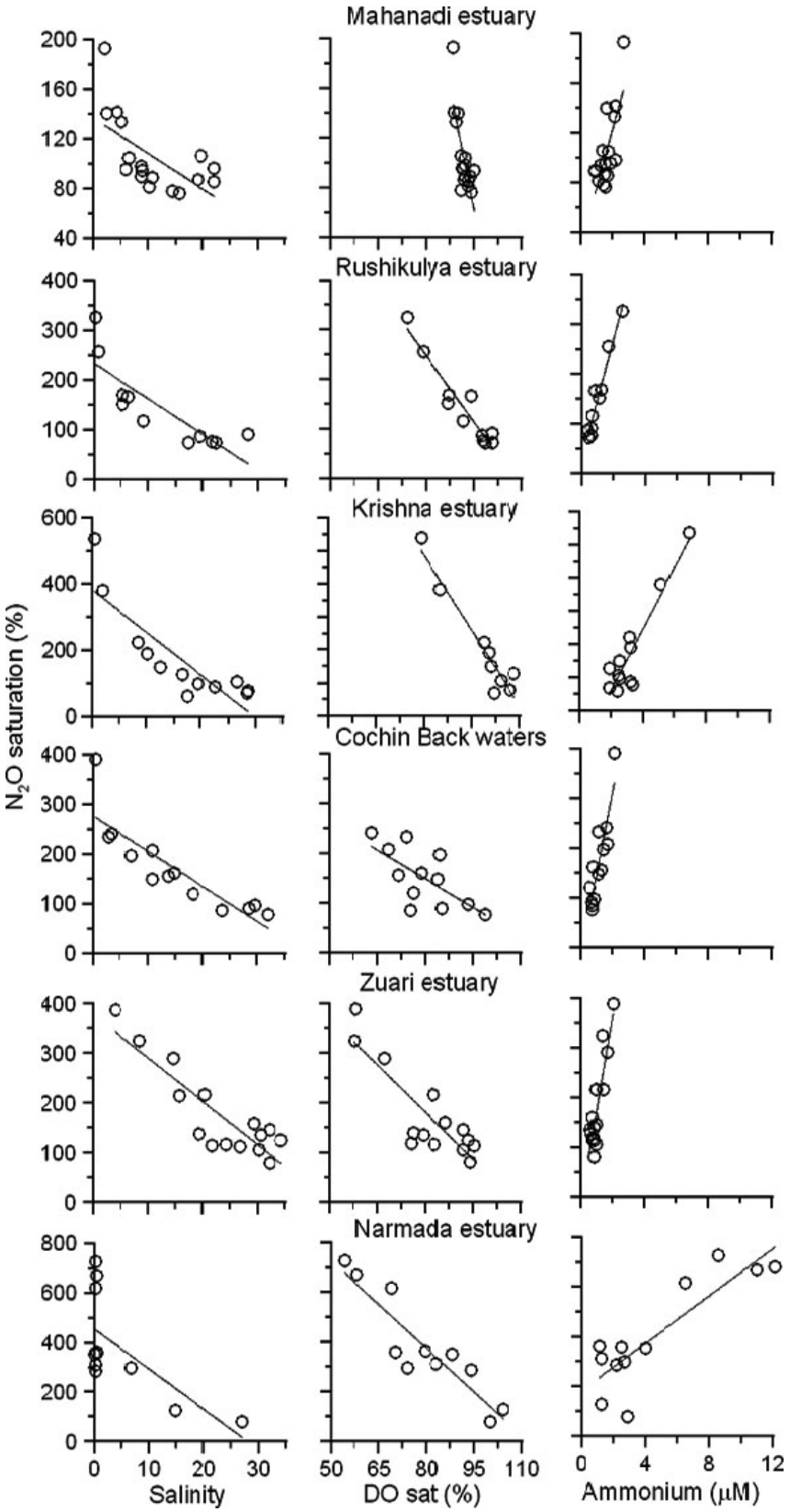

Fig. 4. Relationship of N_2O saturation with salinity, dissolved oxygen saturation and ammonium in selected estuaries.

consumed in states located along the east coast of Indian and ~28% in states located along the west coast and the remaining (~7%) in the central India (Indian Agricultural department, http://indiastat.com/agriculture/2/stats.aspx). On the other hand, lower mean values of pH were found in the west coast estuaries (6.82 ± 0.52) than the east coast estuaries (7.65 ± 0.57), suggesting that further higher nutrients in the former are caused by higher rates of organic matter decomposition and it is consistent with DO saturation. Recently Sarma et al. (2012) found higher pCO_2 levels in the Indian estuaries, which were attributed to organic matter decomposition. Nevertheless, the annual mean N_2O saturation in the Indian estuaries ($204 \pm 137\%$) was significantly less than the European (465%; Bange, 2006 and 271% Barnes and Upstill-Goddard, 2011) and the American estuaries (165–618%; Table S1; supplementary information).

3.2. N_2O emissions from Indian estuaries

The hourly mean wind speed (u_{10}) ranged between 0.31 and 2.66 m s^{-1} during the study period. The seasonal mean wind speed data, prepared from the hourly mean data, were used to compute fluxes. The N_2O efflux from the Indian estuaries ranged between -1.1 and 12.1 μmol m^{-2} d^{-1} during the wet period and between -0.01 and 14.1 μmol m^{-2} d^{-1} during the dry period (Table 1). Higher fluxes were noticed in the Baitharini, Godavari, Ponnayar, Cochin Black waters, Tapti, Nethravathi, Khali and Mondovi estuaries (0.2–14.2 μmol N_2O m^{-2} d^{-1}), while lower fluxes were found in other estuaries (-1.12–5.36 μmol N_2O m^{-2} d^{-1}; Table 1). Such high fluxes in the former estuaries were driven not only by high N_2O levels but also by winds. The mean flux from the Indian estuaries amounts to 1.07 and 1.65 μmol m^{-2} d^{-1} during the wet and dry periods, respectively, with an annual mean of 1.34 μmol m^{-2} d^{-1}.

The annual mean emissions from the Indian estuaries were significantly less than the European estuaries (~2.7 μmol m^{-2} d^{-1}), and they contribute to 0.6% to the world estuaries. Such significant difference might have been caused by variations in DIN loading and nitrification rates. The DIN concentrations in the European and American estuaries were in the range of 5–500 μM (Table S2, supplementary information) with nitrification rates of 0.2–336 μmol N l^{-1} d^{-1}. Higher ammonium concentrations were found in the Shelde estuary, and higher nitrification rates in the Girode estuary (Table S3, supplementary information). On the other hand, ammonium concentrations in the Indian estuaries were 0.6–16.6 μM during the wet period, whereas they were 0.6–13.5 μM during the dry period and these concentrations are significantly less than the world estuaries (Table 1, S3). Sarma et al. (2009, 2010) showed that monsoonal estuaries received significant amount of nutrients during the peak discharge period. However, nutrients are not utilized in the estuary due to high flushing rates and high suspended load (Sarma et al., 2009; Acharyya et al., 2012). As a result, nutrients are flushed to the coastal regions where they support primary production. Hence, low nitrification rates were found during the dry period in the Indian estuaries (0.007 and 0.87 μmol N l^{-1} d^{-1}) compared to world estuaries (0.2–336 μmol N l^{-1} d^{-1}; Table S3).

India houses a total of 14 major, 44 medium and 162 minor estuaries, and the total surface area of Indian estuaries comes to 27 000 km^2 calculated from the mouth of the estuary to the region where tidal oscillations are almost negligible (Qasim, 2003). The weight averaged net annual emission of N_2O from the Indian estuaries amounts to 0.71×10^{-3} and 0.46×10^{-3} Tg N_2O during dry and wet periods, respectively (each of 6 months), and the annual emission amounts to 0.0006 Tg N_2O y^{-1} covering an area of 0.027×10^6 km^2, which is about half of the revised emission estimate from European estuaries (0.012 Tg N_2O y^{-1}; Barnes and Upstil-Goddard, 2011) covering an almost similar area (0.03×10^6 km^2). The fluxes from the Indian estuaries were much smaller (0.01%) compared to world estuaries (4.7 Tg N_2O y^{-1}). Mangroves are a strong source of trace gases to the atmosphere (Chauhan et al., 2008; Krithika et al., 2008; Fernandes et al., 2012). Mangroves are located close to several Indian estuaries. Chauhan et al. (2008) estimated N_2O fluxes from the mangrove located along the east coast of India to be 5.8×10^3 gN_2O y^{-1}. Assuming a similar emission from the west coast, the N_2O emission from the mangrove amounts to an insignificant fraction compared to the fluxes from Indian estuaries.

3.3. Sources of errors on water–air fluxes of N_2O estimations

The errors arise from various sources such as scaling errors arise from the consideration of studied 28 estuaries representing Indian estuaries as a whole, uncertainties from transfer velocity, bias in mean dissolved N_2O values due to low spatial and temporal data resolution. Estimating fluxes to the area representing all estuaries in India may be prone to significant error. We have calculated the flux budget for individual estuaries, where samples were collected, and the mean saturation was used to apply to other Indian estuaries where data were not available. Since other Indian estuaries were mainly minor estuaries and unpolluted, being situated away from the human settlements, their mean N_2O was computed from the data measured in non-polluted estuaries, given in Table 1. However, the calculated areas of

Indian estuaries can have an error of up to 15% (Qasim, 2003). The transfer velocity versus wind speed relations carry low errors at the lower wind speeds (up to 20%), which are normally encountered in our study region (<2 m s^{-1}). Based on our 28 Indian estuaries study, the uncertainty in Indian estuarine N_2O saturations can be 25% (1σ of the estuarine mean) including the uncertainty in N_2O analysis. Using these individual errors, the maximum uncertainty in our N_2O emission estimate for Indian estuaries was up to $\pm 62\%$.

4. Summary and conclusions

The present study reveals that Indian estuaries are a source for atmospheric N_2O. A wide range of N_2O saturation levels were observed in the Indian estuaries varying from 70 to 631% and from 75 to 567% during the wet and dry periods, respectively. Exceptionally high saturation (5902%) was observed only in the Ponnayar estuary during the wet period. The annual mean N_2O saturation in the Indian estuaries ($204 \pm 137\%$) was significantly less than European (271–465%) and American estuaries (165–618%). The mean flux of N_2O from the Indian estuaries amounts to 1.07 and 1.65 μmol N_2O m^{-2} d^{-1} during the wet and dry periods, respectively, with annual mean of 1.34 μmol N_2O m^{-2} d^{-1}, which is significantly less than European estuaries (~ 2.7 μmol N_2O m^{-2} d^{-1}). Such low saturation and fluxes of N_2O in the Indian estuaries were related to mean low concentrations of DIN and nitrification rates compared to world estuaries. Despite the high amount of artificial fertilizers, in terms of nitrogen and phosphorus, used in India which are expected to end up in the estuaries, however, they are little modified within the estuary, due to high flushing rates during the wet period. Sarma et al. (2012) calculated the mean flushing time for the Indian estuaries to be <10 d, whereas it is >40 d for the estuaries from Europe and USA. Hence, microbes are not able to oxidize ammonium efficiently resulting in low nitrification rates in the Indian estuaries. In addition to this, Indian estuaries due to less human settlements along the banks of Indian estuaries receive less domestic and industrial pollution. As a result, Indian estuaries contribute less N_2O to the atmosphere than elsewhere in the world.

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