

Nitrous oxide in the Changjiang (Yangtze River) Estuary and its adjacent marine area: Riverine input, sediment release and atmospheric fluxes

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Abstract. Dissolved nitrous oxide (N₂O) was measured in the waters of the Changjiang (Yangtze River) Estuary and its adjacent marine area during five surveys covering the period of 2002–2006. Dissolved N₂O concentrations ranged from 6.04 to 21.3 nM, and indicate great temporal and spatial variations. Distribution of N₂O in the Changjiang Estuary was influenced by multiple factors and the key factor varied between cruises. Dissolved riverine N₂O was observed monthly at station Xuliujing of the Changjiang, and ranged from 12.4 to 33.3 nM with an average of 19.4 ± 7.3 nM. N₂O concentrations in the river waters showed obvious seasonal variations with higher values occurring in both summer and winter. Annual input of N₂O from the Changjiang to the estuary was estimated to be 15.0×10^6 mol/yr. N₂O emission rates from the sediments of the Changjiang Estuary in spring ranged from -1.88 to $2.02 \mu\text{mol m}^{-2} \text{d}^{-1}$, which suggests that sediment can act as either a source or a sink of N₂O in the Changjiang Estuary. Average annual sea-to-air N₂O fluxes from the studied area were estimated to be 7.7 ± 5.5 , 15.1 ± 10.8 and $17.0 \pm 12.6 \mu\text{mol m}^{-2} \text{d}^{-1}$ using LM86, W92 and RC01 relationships, respectively. Hence the Changjiang Estuary and its adjacent marine area are a net source of atmospheric N₂O.

1 Introduction

N₂O is an important trace gas in the atmosphere, which is responsible for 5–6% of the greenhouse effect (Houghton et al., 1996), and also contributes to the destruction of the ozone layer (Crutzen and Schmailzl, 1983). The global atmospheric N₂O concentration has increased from a pre-industrial value of about 270 to 319 ppb in 2005 (IPCC, 2007). The oceans are considered to be significant sources for atmospheric N₂O, contributing about 25% of the global emissions (Nevison et al., 1995; Bouwman et al., 1995). However, emission of N₂O from the oceans is not uniformly distributed geographically. Estuaries have been subject to intense anthropogenic inputs of inorganic nitrogen as a consequence of fertilizer usage and sewage input over recent decades (Howarth et al., 1996). One important consequence of the increased N load is the enhanced production and emission of N₂O from estuaries (Barnes and Owens, 1998; De Wilde and de Bie, 2000; Marty et al., 2001; LaMontagne et al., 2003; Garnier et al., 2006). Although estuaries represent only about 0.4% of the global ocean area, Bange et al. (1996) estimated they account for about 33% of the oceanic N₂O emission. However, these estimates are rather uncertain due to high spatial and temporal variability and the limited data available, especially for the typical large river estuaries in the world. For example, very limited data are available for the Amazon, the Mississippi and large river estuaries in Asia.

The Changjiang (Yangtze River), 6300 km at total length, is the largest river in Asia, ranking third in length, fifth in freshwater discharge and fourth in sediment discharge among the world's rivers (Milliman and Syvitski, 1992). Its drainage



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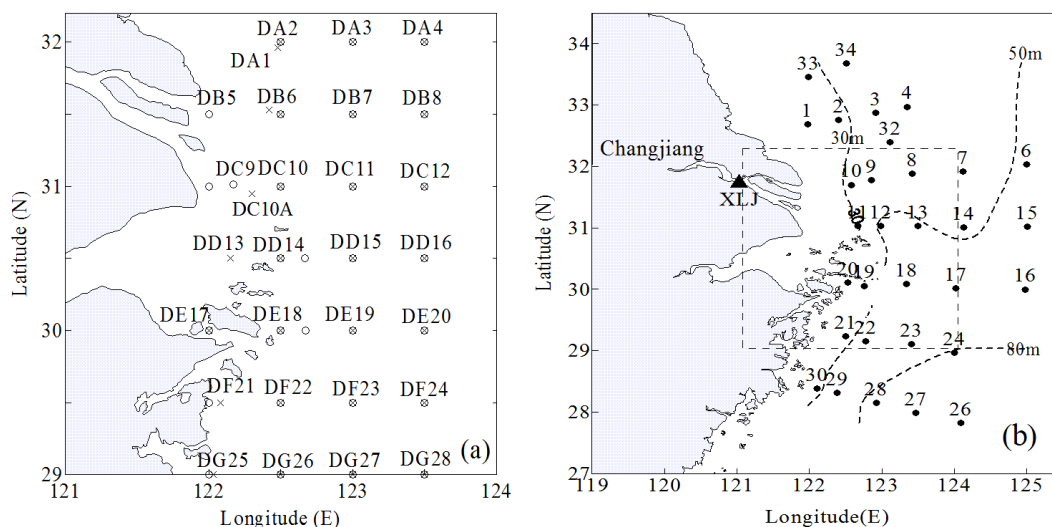


Fig. 1. Sampling locations in the Changjiang (Yangtze River) Estuary. (a) April (x) and November (o) of 2002; (b) June, August, October of 2006 (●) and Xuliujing (XLJ, solid triangle); The box in (b) indicates the area covered by (a) and the dashed lines indicate the isobaths.

basin covers about 1.8 million km² in area, which is about one fifth of the total land area of the whole country. The huge amount of runoff discharge (903 km³/yr averaged from the 1950s to 2005), and sediment load (414 million t/yr averaged from the 1950s to 2005) enter its estuary and are emptied into the East China Sea (ECS) (Wang et al., 2008). The Changjiang estuary is of particular interest to nutrient cycling because of its importance for the transportation of terrigenous nutrients to the coastal seas. The annual dissolved inorganic nitrogen (DIN) concentrations and fluxes from the Changjiang show a stable to slowly increasing trend from the 1950s to the early 1980s, but then increased abruptly (Liu et al., 2003; Li et al., 2007). For example, the nitrate concentration near the mouth of the Changjiang has increased from ~60 μmol/L in the 1980's to ~80 μmol/L in 1997 (Liu et al., 2003). The DIN flux from the Changjiang has increased from (0.3~0.5) × 10⁶ t/yr in 1970–1980 to (1.2~1.5) × 10⁶ t/yr in late 1990s (Li et al., 2007; Zhang et al., 2003). The dissolved organic nitrogen (DON) and particulate nitrogen (PN) concentrations were 22.5 ± 19.6 and 9.1 ± 4.0 μmol/L at Datong station in the Changjiang, and DON and PN fluxes were estimated to be 0.47 × 10⁶ and 0.16 × 10⁶ t/yr during 1998–1999 (Zhang et al., 2003). On a global scale, half of the total nitrogen load received by estuaries has been estimated to be removed by denitrification (Nixon et al., 1996). The Changjiang Estuary exhibits turbidity maximum at the mouth (Li and Chen, 1998), which is likely to have a significant impact on nitrification in the turbidity maximum (Law et al., 1992). Considering both nitrification and denitrification can produce N₂O, the increasing load of nitrogen (DIN, DON and PN) to the Changjiang Estuary may potentially affect the cycling of N₂O, its subsequent emission to the atmosphere and to the open sea as well. However, no data are so far avail-

able for the distribution, fluxes and production processes of dissolved N₂O in the Changjiang Estuary. Hou et al. (2007) studied the N₂O production in the intertidal sediments of the Changjiang Estuary, and found that N₂O was mainly from nitrification under the aerobic condition and from denitrification under the waterlogged and reflooded conditions.

Here we present a study on the distribution of N₂O in the outer estuary of the Changjiang and its adjacent marine areas. The objectives of our study were: (1) to determine the distribution of N₂O along the Changjiang Estuary; (2) to estimate the N₂O emission into the atmosphere; (3) to evaluate the contribution of the Changjiang River to N₂O in the estuary.

2 Methods and materials

2.1 Sample collections

Five cruises were conducted on the outer estuary of Changjiang and its adjacent area during 25 April–15 May 2002 by R/V “Haijian 47”, 4–14 November 2002 by R/V “Science No. 1”, during 2–11 June, 19–31 August and 3–13 October 2006 by R/V “Beidou”, respectively. The sampling locations are shown in Fig. 1.

Water samples were collected using 10L Niskin bottles. Subsamples for N₂O determination were transferred from Niskin bottles into 135 mL or 60 mL glass vials using the rubber-connecting tube with a glass pipette end. After overflow of approximately 1.5 to 2 fold of bottle volume, saturated solution of HgCl₂ was added to inhibit microbial activity, then the sample vial was immediately sealed with a butyl rubber stopper and an aluminum cap to exclude the excessive water and stored in the dark box. All the water samples were analyzed after returning to the shore laboratory

within 60 days of collection. Data of temperature, salinity and dissolved oxygen were obtained from the shipboard CTD profiles.

To quantify the flux of N_2O input to the sea from the Changjiang, N_2O concentrations were monitored monthly at Xuliujing ($121^\circ 2' E$, $31^\circ 46' N$, Fig. 1b), the most downstream main channel station, from June 2007 to May 2008. Xuliujing is influenced by tide but the salinity is 0 all year around and the surface water usually contains high level of dissolved oxygen, ranging from 8.3 to 10.3 mg/L (Fan and Xu, 2007). Since it is located at the further upstream side from limit of salt water intrusion during dry seasons and at the node where the river estuary begins to become wide, Xuliujing is suitable for observing the freshwater input to the sea from the Changjiang. Water samples were collected using 10L bucket. Subsamples for N_2O determination and the treatment of water samples were the same as above. All the water samples were analyzed within 2 month after collection.

Sediment cores were sampled using a multiple corer (each sediment core 60 cm long and 10 cm I.D.) from stations DC10 and DB6 (Fig. 1a) in the Changjiang Estuary during the spring cruise in 2002. After collection, the cores with 20–30 cm of sediments were selected and left undisturbed in the plexiglass tubes with the end sealed with air-tight rubber bungs in dark before the determination of trace gas release.

2.2 Chemical analysis

Dissolved N_2O was measured by gas chromatography using a gas-stripping method (Zhang et al., 2006). Calibration of the Electron Capture Detector (ECD) responses were done by injection of certain volumes of standard gas of 5.60 ppmv N_2O/N_2 (Research Institute of China National Standard Materials) into the stripper filled with blank seawater. The N_2O of the blank seawater had previously been stripped out together with other dissolved gases by ultra-pure N_2 . After injection, the blank seawater was subsequently analyzed by the same procedure used for unknown samples. The method detection limit (MDL) for N_2O analysis in this study was 0.1 nmol/L (MDL is defined as the N_2O concentration in 135 mL seawater sample corresponding to two standard deviations of seven replicates of the blank), respectively. The precisions of repeated analysis of water samples were about 5% for N_2O in routine sample analysis.

Water samples for determination of nutrients were filtered through acid-cleaned acetate cellulose filters (pore size: 0.45 μm). Microbial activity in filtrates was inhibited by $HgCl_2$ and then stored in the dark at 4 °C. In the laboratory, nutrients were determined photometrically by an auto-analyzer (Model: Skalar SAN^{plus}) with precision of <5–10%.

2.3 Measurements of sediment-water N_2O fluxes

Sediment-water N_2O fluxes from the Changjiang Estuary were determined using the closed chamber technique (Barnes and Owens, 1998) during April/May 2002. Measurements were conducted immediately after core collection. After removing the overlying waters carefully without disturbing the biological activity, filtered bottom waters were added carefully without gas phase left. The top of the tubes was then sealed with air-tight rubber bungs equipped with two stopcocks. An aerated pump was put in half of the water phase to stir the water phase. During 2 days incubation experiments, overlying water samples were carefully taken out at different time intervals through one stopcock fitted in the rubber bung for determination of dissolved O_2 , and N_2O changes in the enclosed water phase. The water overlying the core was replenished simultaneously via another stopcock fitted with a syringe containing filtered bottom water. No air was involved during these processes. After each sampling, two bottles of filtered bottom water using as replenishment were collected for determination of the N_2O concentration to correct the N_2O change of the overlying water. The dissolved N_2O in the overlying water were analyzed using the gas-stripping method described above. The dissolved O_2 was measured by a DO probe Model 9101Y (Jenco, USA). The sediment-water N_2O fluxes were determined from the slope of the N_2O increase/decrease in the overlying water versus incubation time. All incubation experiments were performed in duplicate, and the results are reported as the mean values.

2.4 Computation of sea-to-air fluxes

Sea-to-air N_2O fluxes (F in $mol\ m^{-2}\ d^{-1}$) can be estimated by the following equation

$$F = k \cdot (C_{obs} - C_{eq}) \quad (1)$$

Where C_{obs} is the observed concentration of dissolved N_2O ; C_{eq} is the air-equilibrated seawater N_2O concentration, which was calculated for in situ temperatures and salinities using the solubility data of Weiss and Price (1980). Atmospheric N_2O was not measured during these cruises, and a global mean atmospheric N_2O mixing ratio of 317.6 ppb for 2002 and 320.3 ppb for 2006 from the NOAA/ESRL halocarbons in situ program (<http://www.esrl.noaa.gov/gmd>) was used for the calculations in this study. k is the transfer velocity of the gas indicated, which is usually expressed as a function of the wind speed and the Schmidt Number (Sc). Various empirical relationships have been derived for estimating k . The two most widely used are those of Liss and Merlivat (1986) and Wanninkhof (1992), which are often assumed to define the lower and upper limits for k . However, tidal currents may also contribute to water turbulence, especially in inner estuaries with shallow waters and high frictions on the bottom (Raymond and Cole, 2001; Zappa et al., 2003; Abril and Borges, 2004). Raymond and Cole (2001) derived

Table 1. Observed N₂O, temperature, salinity and O₂ in surface and bottom waters of the Changjiang Estuary and its adjacent area (Numbers in the parentheses are the saturations in %; O₂ data for Nov 2002 is not available due to technical troubles).

Date	Stations	Surface	Surface	Surface O ₂	Surface N ₂ O	(nM)	Bottom	Bottom	Bottom O ₂	Bottom N ₂ O	(nM)
		temperature (°C)	salinity	(mg/L)	Range	Mean ± S.D.	temperature (°C)	salinity	(mg/L)	Range	Mean ± S.D.
25 Apr–3 May 2002	28	17.4 ± 1.1	28.9 ± 6.6	8.7 ± 0.7 (108 ± 6)	8.17–18.9 (103–221)	11.77 ± 2.15 (141 ± 23)	17.5 ± 0.9	31.4 ± 3.3	7.8 ± 1.3 (96 ± 16)	8.49–14.3 (108–187)	12.0 ± 1.34 (147 ± 17)
4–11 Nov 2002	30	19.4 ± 1.6	27.7 ± 5.3		6.59–16.7 (84–200)	9.00 ± 2.11 (114 ± 25)	17.5 ± 0.9	30.1 ± 4.6		5.83–18.2 (81–220)	9.38 ± 2.13 (125 ± 26)
2–11 Jun 2006	25	20.1 ± 2.2	30.6 ± 2.3	5.7 ± 0.6 (73 ± 7)	7.48–10.68 (110–135)	9.10 ± 0.88 (119 ± 6)	18.1 ± 2.3	32.6 ± 1.6	3.9 ± 1.0 (48 ± 11)	9.28–16.10 (110–203)	11.03 ± 1.87 (138 ± 26)
15–31 Aug 2006	30	28.9 ± 0.9	31.2 ± 2.2	4.9 ± 0.8 (72 ± 13)	6.04–21.32 (101–363)	10.78 ± 4.25 (184 ± 71)	21.4 ± 3.5	33.2 ± 1.4	2.4 ± 1.0 (32 ± 14)	6.67–20.72 (70–259)	9.66 ± 3.13 (134 ± 44)
3–13 Oct 2006	30	24.5 ± 1.0	32.5 ± 1.5	5.0 ± 0.6 (69 ± 9)	6.90–13.49 (106–201)	10.11 ± 1.56 (153 ± 24)	22.5 ± 2.0	33.2 ± 1.3	3.9 ± 0.8 (52 ± 12)	6.75–18.44 (99–245)	11.80 ± 2.42 (169 ± 32)

a relationship ($k_{600} = 1.91 \exp(0.35u_{10})$, u_{10} is the wind speed at a height of 10 m) based on a compilation of published k_{600} (the transfer velocity for CO₂ at 20 °C in freshwater) values in various rivers and estuaries and obtained using different methods (floating chamber, natural tracers (CFC, ²²²Rn), and added tracer (SF₆)). Their studies suggested that k could be significantly higher in estuaries than in open oceanic waters at the same wind speed. Since no direct measurements of gas transfer velocity were made in the Changjiang Estuary, the relationships of Liss and Merlivat (1986) (hereafter referred to as LM86), Wanninkhof (1992) (hereafter referred to as W92) and Raymond and Cole (2001) (hereafter referred to as RC01) were used to compute k to help comparisons with published data. The transfer velocity was adjusted by multiplying with $(Sc/600)^{-n}$ for LM86 ($n = 1/2$ for wind speed > 3.6 m/s and $n = 2/3$ for wind speed < 3.6 m/s), $(Sc/660)^{-1/2}$ for W92, and $(Sc/600)^{-1/2}$ for RC01, where Sc is the Schmidt number for N₂O and was calculated according to the equation by Wanninkhof (1992).

The major uncertainty in the assessment of sea-to-air gas fluxes is related to the estimation of the gas transfer velocity, which depends on the type of wind data used. In this work, we computed the gas transfer velocity using averaged monthly wind speeds obtained from the monitoring results beyond the Changjiang Estuary in 1977–1986, which was 6.7 m/s for May, 6.8 m/s for June, 7.6 m/s for August, 7.2 m/s for October and 7.6 m/s for November (cf. Xu, 1992). Since during the May 2002 and October 2006 cruises, wind speeds were continuously recorded shipboard using an automated weather station (Campbell Scientifics, UK), the gas transfer velocities and sea-to-air fluxes were also estimated using ship based in situ wind speeds to help comparisons.

3 Results and discussion

3.1 Distributions of N₂O in the Changjiang Estuary and its adjacent area

N₂O concentrations and saturations in the surface and bottom waters of the Changjiang Estuary and its adjacent area during five cruises from 2002 to 2006 are shown in Table 1, and indicate great temporal and spatial variations. The horizontal distributions of N₂O concentrations in the Changjiang Estuary and its adjacent area are shown in Fig. 2. Generally high N₂O concentrations were observed beyond the mouth of the Changjiang and Hangzhou Bay, especially in the bottom waters. N₂O concentrations showed no significant correlation with salinity in this study (Fig. 3). Similar phenomenon has been observed by Amouroux et al. (2002) in the surface water of the north-west Black sea shelf and by Bange et al. (1998) in the estuarine and coastal waters of southern Baltic Sea. However, N₂O concentrations in the Changjiang estuary were found to correlate well with salinity in September 2003 ($[N_2O] = -0.87s + 38.2$, $r^2 = 0.79$, $n = 25$, Zhang et al., 2008). This may be because that only high salinity area was covered in this study and N₂O data were scattered due to ventilation to the atmosphere and the influence of internal (i.e. nitrification and denitrification) and external processes (i.e. freshwater input and mixing of different water masses). For example, the water discharge of Changjiang in August 2006 (27 600 m³/s) and October 2006 (14 800 m³/s) is 38% and 55% lower than the long-term monthly average water discharge of 44 570 and 35 550 m³/s for August and October. Hence the influence of N-rich freshwater was rather limited in this study. The distribution of N₂O in the Changjiang estuary was also influenced by oxygen levels. It can be seen from Table 1 that during the 3 cruises in 2006, oxygen deficiency occurred to different extent in the bottom waters of Changjiang Estuary. The apparent N₂O production (ΔN_2O) correlated well with apparent oxygen utilization (AOU) in the cruises of June and October 2006 (Fig. 4), but no obvious correlation was observed for the cruise in August, suggesting the influence

Table 2. Summary of N₂O measurements in various estuaries in the literatures.

Study Area	Stations	Date	Sur. N ₂ O, (nM)	Sur. R, (%)	Salinity	Flux (μmol-m ⁻² .d ⁻¹)	Ref.
Danube River plume	25	Jul–Aug 1995	(8.0 ± 1.0)	(112)	8.5–18.5	(1.6 ^a); (2.8 ^b)	Amouroux et al. (2002)
Rhone River plume	9	Jun 1998	16.76–41.04				Marty et al. (2001)
Tamar estuary	18 ^c	Aug 1988	9–30 ^c		0–30 ^c	(12)	Law et al. (1992)
	29 ^c	Oct 1988	9–24 ^c		0–30 ^c	(11)	
	22 ^c	Mar 1989	15–23 ^c		0–20 ^c	(11)	
	22 ^c	Jun 1990	10–18 ^c		0–30 ^c	(8.4)	
Humber estuary	11 ^c	Mar–Dec 1996		100–4250 (452)	0–30		Barnes and Owens (1998)
Tweed estuary		Sep 96–Mar 97		96–110(100.4)			
Gironde estuary	9	Nov 1991	(14.3)	106–165 (132)	5–34		Bange et al. (1996)
Loire estuary	13	Jun 1997	9.8–36.7		0–30		De Bie et al. (2002)
		Sep 1998	7.3–21		0–32		De Bie et al. (2002)
Schelde estuary	15	Oct 1978	10–250	120–3000(1560)	0–30		de Wilde and de Bie (2000)
	35 ^c	Oct 1993	10–338		2–30		
	22 ^c	Mar 1994	75–150		2–10		
		Jul 1996	50–300		2–22		
Schelde estuary	10	May 97–Apr 98	8.7–1457	(710)	0–25		de Bie et al. (2002)
Thames estuary	15	Feb 1998	11.2–93	93–681 (321)	0–33		
Colne estuary		Aug, Nov 2001; Feb, May 2002	(197.3 ± 24.9)	(993 ± 120)		(266 ± 243)	Dong et al. (2004)
		Aug, Nov 2001; Feb, May 2002	(46.3 ± 3.9)	(282 ± 26)			Dong et al. (2004)
Colne estuary		May 2002	467.5	2187		685.5	Robinson et al. (1998)
Seine River estuary		Summer				39–98	Garnier et al. (2007)
Changjiang estuary	3	Sep 2003	(31.44 ± 4.56)	(455 ± 56)	0.6–13.5	(87 ± 35) ^a ; (141 ± 56) ^b	Zhang et al., 2008
Changjiang estuary	3–16	2002–2006	(10.21 ± 1.75)	(137 ± 20)	14–30	(6.8 ± 3.7) ^a ; (13.3 ± 7.2) ^b	This study
Pearl River estuary	14	Sep 2003	20.4–48.6		0–5		Chen et al. (2008)
Temmesjoki estuary	3	Summer 2004	7.3–15	136		5–7	Silvennoinen et al. (2008)

^a K_w was estimated by the LM86 equation; ^b K_w was estimated by the W92 equation; ^c The values were estimated according to the figures in the reference. Numbers in the parentheses are the average value.

of oxygen is more complicated than expected. The distribution of N₂O in the Changjiang estuary was also influenced by other environmental factors. For example, N₂O concentrations correlated with nitrate ([N₂O] = 0.21[NO₃⁻] + 8.6, *n* = 120, *r*² = 0.35) and temperature ([N₂O] = 0.65 *t* + 26.6, *n* = 120, *r*² = 0.24) in June 2006. N₂O concentrations in bottom waters correlated well with suspended particulate matter (SPM) ([N₂O] = 0.01 SPM + 8.0, *n* = 30, *r*² = 0.49) in November 2002. All these results suggest that N₂O distribution in the Changjiang Estuary was influenced by multiple factors. The influence of these factors is not inclusive but additive and the key factor varied between different cruises depending on environmental conditions. But the regulation mechanism of these factors are far beyond discussion in this study due to limited data. Hence more research on the Changjiang Estuary at different temporal and spatial scales is needed to characterize the distribution of N₂O and the controlling factors. More direct examination of nitrogen cycling processes (e.g., nitrification and denitrification rates) within the water and sediment system is needed to fully understand the biogeochemical cycles of N₂O.

Table 2 shows previously published data on N₂O in other estuaries, which indicates that N₂O concentrations vary over a wide range of 2–1457 nM at various temporal and spatial scales. N₂O in the outer estuary of Changjiang and its adjacent marine area falls within this range but toward the low end. This may be partly due to the fact that most previously

published N₂O data in Table 2 covered the full salinity range of 0–30 while N₂O data in this study were mainly from the high salinity area (salinity of 20–30) of the Changjiang Estuary. High N₂O were usually observed at the inner estuaries, especially at the low salinity in the vicinity of turbidity maximum zone (TMZ) (Barnes and Owens, 1999; Law et al., 1992; Abril et al., 2000). Turbidity maximum existed all year round in the river mouth of the Changjiang (Li and Chen, 1998). However, given that the sampled salinity range was mainly limited to high salinity and the TMZ was not covered during all surveys, observed N₂O concentrations in this study only represent the low N₂O levels in the outer Changjiang Estuary. For example, high concentrations of N₂O, ranging from 26.04 to 37.20 nM with an average of 31.44 ± 4.56 nM, were found at the low salinity area (salinity of 0.6–13.5) near the mouth of the Changjiang estuary in September 2003 (Zhang et al., 2008). The observed N₂O concentrations in the outer Changjiang Estuary in this study were comparable to those reported for the Danube river plumes (Amouroux et al., 2002), but lower than those for the Rhone River plume (Marty et al., 2001). On the other hand, N₂O can be produced via both nitrification and denitrification in rivers and estuaries, which was related to external inputs of nitrogen to these systems. Concentrations and emissions of N₂O in estuaries are generally found to be related to the estuarine dissolved inorganic nitrogen (DIN) levels (Seitzinger and Kroeze, 1998; Dong et al., 2004). Mean

Table 3. Compilation of dissolved N₂O in various rivers (numbers in the parentheses are the averaged value).

Rivers	Description	N ₂ O (nM)	N ₂ O (%)	Ref.
Alsea River	Oct 1979	8.2–15.6	94–166	De Angelis and Gordon (1985)
South Platte river	Jan/Feb 2000	18–527 (59)	2500	Dennehy and McMahon (2000)
Arkansas River	Jan/Feb 2000	3.3–5.9 (3.6)		
Potomac River	Jul/Sep, 1977	7–350	100–5000	McElroy et al. (1978)
Hudson River	1998–1999, monthly measurement	(19 ± 8)	125–385 (185. ± 43)	Cole and Caraco (2001)
English rivers				Dong et al. (2004)
Colne	Aug 2001–May 2002	(44.2 ± 5.0)	(272.5 ± 32.1)	
Ouse	Aug 2001–May 2002	(39.2 ± 2.9)	(217.9 ± 16.5)	
Trent	Aug 2001–May 2002	(43.2 ± 3.5)	(228.4 ± 18.3)	
Stour	Aug 2001–May 2002	(53.9 ± 4.5)	(297.4 ± 25.7)	
Orwell	Aug 2001–May 2002	(60.1 ± 5.4)	(389.1 ± 31.7)	
Amazon River	Mainstem	(13.4 ± 2.5)		Richey et al. (1988)
Millstone River	Mar–May 2002	11.45–13.30	104–123	Laursen and Seitzinger (2004)
Iroquois River	Apr–Jun 2002	13.65–27.67	134–209	
Changjiang	Aug 2002	9.02 ± 1.03		Yan et al. (2004)
	Oct 2002	13.39 ± 8.71		
	Jan 2008	22.0 ± 3.5	168 ± 27	Zhao et al. (2009)
	Jun 2007–May 2008	19.4 ± 7.3	213 ± 97	This study
Pearl River	Sep 2003	20–40		Chen et al. (2008)
	Apr 2004	62–323 (143)	720–4080 (1730)	Xu et al. (2005)
River Temmesjoki	2003–2004	6.7–53 (19)		Silvennoinen et al. (2008)

DIN concentrations in the Changjiang estuary in this study were 12.5 ± 5.8 , 12.6 ± 8.6 and $15.6 \pm 8.0 \mu\text{M}$ for June, August and October 2006, respectively. Although the correlation between N₂O concentrations and DIN was not obvious at most cruises, N₂O and DIN data in the Changjiang Estuary fit well in the plot of estuarine N₂O versus DIN on a global scale (Fig. 5), suggesting that the low N₂O observed in this study is consistent with the low DIN levels. In any way, this study highlights the importance of studies on the N₂O variability of more representative estuaries in the future research to estimate accurately the contribution of estuaries to atmospheric N₂O.

3.2 Riverine input of N₂O

Figure 6 shows the seasonal variation of dissolved N₂O observed at Station Xuliujing during the period of 2007–2008, which ranged from 12.4 to 33.3 nM with an average of 19.4 ± 7.3 nM. N₂O concentrations in the river waters showed obvious seasonal variations with higher values occurring in both the summer and winter. The total suspended matter in surface waters ranged from 12.4 to 143.2 mg/L with an average of 39.5 ± 34.4 mg/L. The observed temperature ranged from 5.0 to 30.0 °C with an average of 19.7 ± 8.5 °C. N₂O concentrations correlate negatively with the in situ temperature ($[\text{N}_2\text{O}] = -0.48t + 27.2$, $r^2 = 0.45$, $n = 11$, July 2007 is not included) while N₂O saturations showed weak positive correlation with the temperature ($\text{N}_2\text{O}(\%) = 5.3t + 109.5$, $r^2 = 0.21$, $n = 12$). This

suggest that the high N₂O concentrations in winter may be partly due to higher N₂O solubility at lower temperatures. The DIN at surface waters of Xuliujing ranged from 101.6 to 156.1 μM with an average of $130.7 \pm 17.9 \mu\text{M}$, among which nitrate is the dominate species with an average of $122.1 \pm 17.1 \mu\text{M}$ and contribute 75%–99% to DIN. N₂O concentrations correlate positively with DIN ($[\text{N}_2\text{O}] = 0.23\text{DIN} - 10.6$, $r^2 = 0.32$, $n = 12$). Table 3 compiled previously published N₂O concentrations and saturations in various world rivers. It can be seen that N₂O concentrations in river waters show great spatial and temporal variations with the range from 3.3 to 527 nM. N₂O concentrations in the surface waters of the Changjiang in this study fall within the reported N₂O ranges in the worldwide rivers. N₂O in the river waters may come from in situ production by nitrification or denitrification (Yan et al., 2004), production and emission by the sediment (García-Ruiz et al., 1999), runoff and ground water from agricultural soils (McMahon and Dennehy, 1999). For example, Yan et al. (2004) reported a N₂O production rate of 1.30 ± 0.85 and $346 \pm 261 \text{ nmol N m}^{-2} \text{ h}^{-1}$ by denitrification in the Changjiang for August and October 2002, respectively. They also observed N₂O concentrations of 9.02 ± 1.03 nM in August 2002 and 13.39 ± 8.71 nM in October 2002 at station Datong (Yan et al., 2004). A survey of the mainstream of Changjiang in January 2008 showed that N₂O concentrations from station Yichang to Xuliujing ranged from 16.6 to 30.7 nM with an average of 22.0 ± 3.5 nM (Zhao et al., 2009). Our

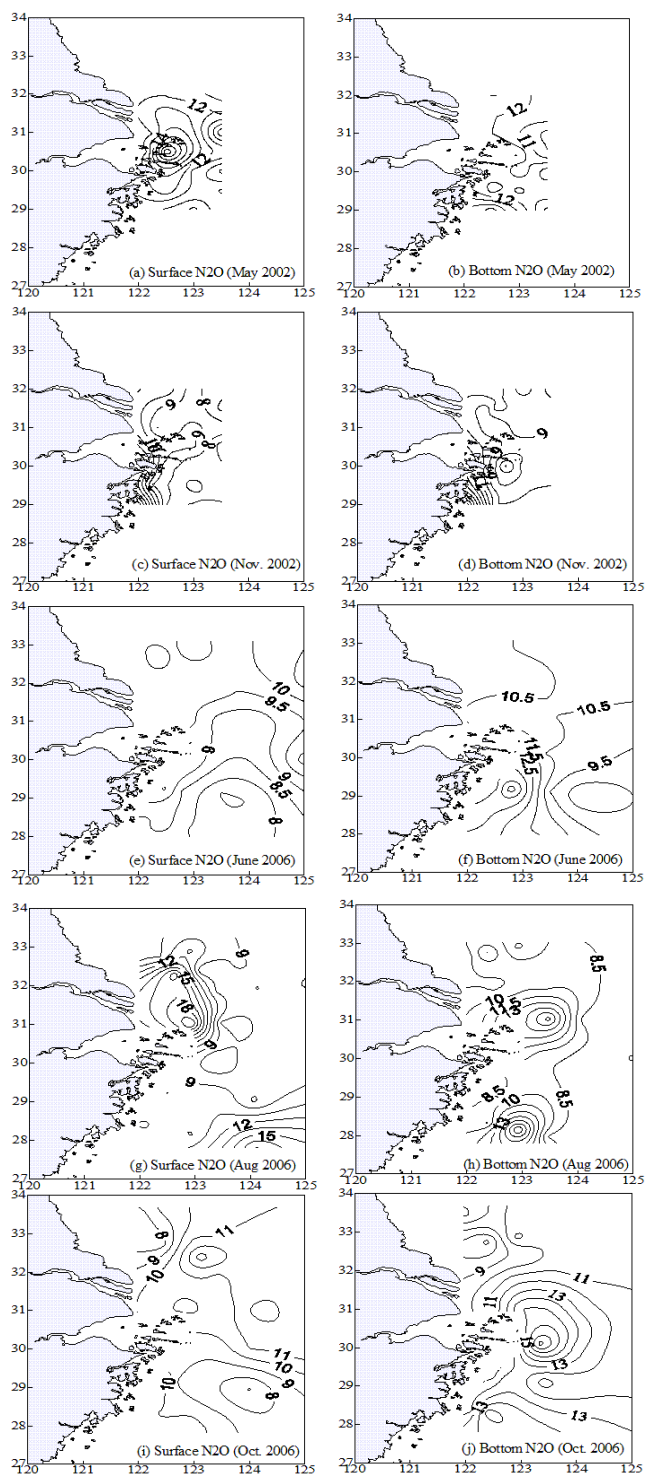


Fig. 2. Horizontal distributions of N_2O in the surface and bottom waters of the Changjiang Estuary.

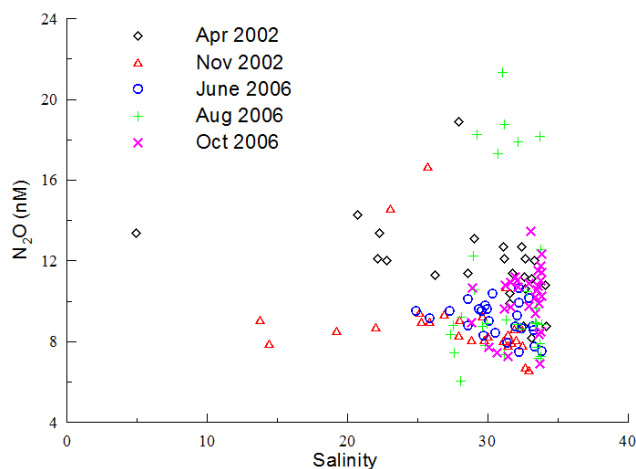


Fig. 3. Surface N_2O concentrations versus salinity in the Changjiang Estuary.

results are comparable to these previously published data for Changjiang.

Since no regular monitoring of flow rates were made at Station Xuliujing, flow rates at Station Datong (about 600 km upstream from Xuliujing) were usually used to represent the water discharge to the sea from the Changjiang. We estimate the annual average input of N_2O from the Changjiang to the estuary by multiplying the monthly river water N_2O concentration by the monthly flow rate, which yields a N_2O flux of 0.5 mol/s equal to 15.0×10^6 mol/yr for the annual input. N_2O input via Changjiang contributes about 7% to the N_2O emission from the estuary (see below), and is a minor source for dissolved N_2O in the Changjiang Estuary.

3.3 Sediment-water N_2O fluxes

In estuarine and coastal regions, the sediments are likely to be important sources of N_2O emitted to the water column since they are active sites for both nitrification and denitrification (Capone, 1991; Barnes and Owens, 1998; Robinson et al., 1998; Usui et al., 2001). A review by Capone suggests the fluxes from the sediments (predominantly in coastal areas) could account for over 40% of the net oceanic N_2O production (Capone, 1991). High nutrient loading from terrestrial environments together with a close benthic and pelagic coupling due to shallow water depth stimulates microbial processes including N_2O production (Seitzinger and Nixon, 1985; Middelburg et al., 1995; Bange et al., 1996; Seitzinger and Kroeze, 1998). Since the Changjiang estuary contains large amount of dissolved nitrogen species, one would expect high production and release of N_2O from the sediments.

Incubation experiments at stations DC10 (Clay, depth 10 m) and DB6 (Silt, depth 23 m) in May 2002 showed different results. Obvious accumulation of N_2O together with the decrease of O_2 in the overlying water was observed

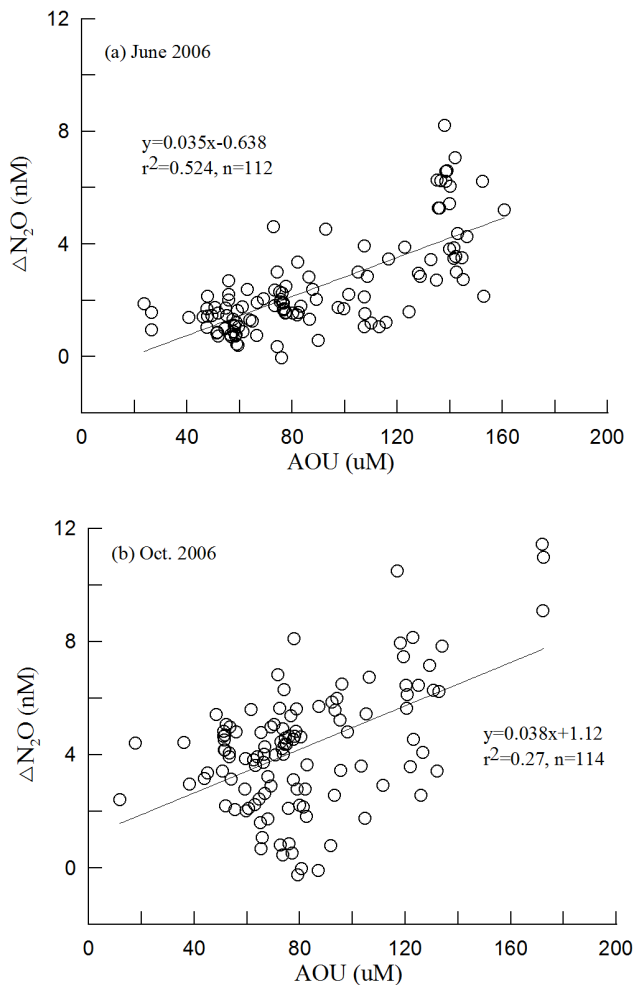


Fig. 4. Relationship between the apparent N_2O production ($\Delta\text{N}_2\text{O}$) and apparent oxygen utilization (AOU) in the Changjiang Estuary.

during sediment incubation at station DB6 (Fig. 7). Sediment oxygen consumption rates and N_2O effluxes from the sediments were calculated to be $32.9 \text{ mmol m}^{-2} \text{ d}^{-1}$ and $2.02 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$, respectively. Incubation experiments of nutrient exchange between sediment-water interface under oxic environments showed that nitrate was transferred from the sediment to water column, while NH_4^+ was transferred from the water column to sediment at station DB6 (Qi et al., 2003). Since the dissolved oxygen in bottom water of station DB6 is highly saturated (104%, 9.54 mg/L) and the sediment type is silt, high availabilities of O_2 and NH_4^+ provide favorable conditions for the occurrence of nitrification in the sediments. Hence N_2O may be produced mainly via nitrification in the surface sediments at station DB6 and then released to the water column together with the produced nitrate. During the 4h incubation at station DC10 both N_2O and O_2 in the overlying water decreased. Sediment oxygen consumption rates and N_2O effluxes from the sediments were calculated

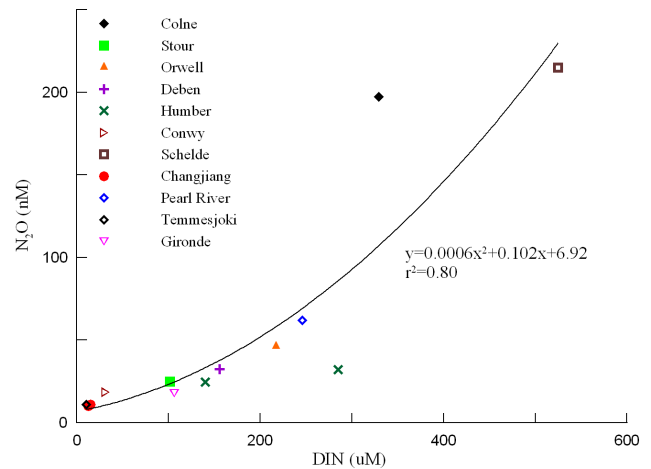


Fig. 5. N_2O concentrations versus DIN for various estuaries (The data were from this study and the references in Table 2).

to be $66.8 \text{ mmol m}^{-2} \text{ d}^{-1}$ and $-1.88 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$, respectively, for station DC10. Incubation experiments of nutrient exchange between sediment-water interface under oxic environments showed that both nitrate and NH_4^+ was transferred from the water column to sediment (Qi et al., 2003). Since the bottom water of station DC10 is characterized of low dissolved oxygen (4.41 mg/L) and the sediment is clay, O_2 is not easily transferred to the sediment. These suggest that N_2O can be produced via both nitrification and denitrification in the sediment at station DC10, but the occurrence of N_2O reduction simultaneously with the production by denitrification induced net consumption of N_2O in the sediment. Li et al. (2009) reported that the sediment denitrification rates ranged from 101.3 to $731.9 \text{ } \mu\text{mol N}_2\text{O m}^{-2} \text{ h}^{-1}$ in June 2006 in the Changjiang Estuary.

Previous studies showed that benthic N_2O fluxes from sediments showed highly temporal and spatial variations (-5 to $600 \text{ } \mu\text{mol N}_2\text{O m}^{-2} \text{ d}^{-1}$; Kieskamp et al., 1991; Barnes and Owens, 1998; Usui et al., 1998; Laursen and Seitzinger, 2002). Benthic N_2O fluxes obtained in this study fell within the general range, and were consistent with those reported for Mid-Atlantic bight ($-1.82 \sim 2.03 \text{ } \mu\text{mol N}_2\text{O m}^{-2} \text{ d}^{-1}$), which also showed highly variable in both magnitude and direction of N_2O flux (Laursen and Seitzinger, 2002). However, our results were lower than those reported by Wang et al. (2007) for the intertidal sediments of the Changjiang Estuary in summer ($1.2 \sim 102 \text{ } \mu\text{mol N}_2\text{O m}^{-2} \text{ d}^{-1}$). High N_2O emission rates from the intertidal sediments may be resulted from the increase supplies of nutrients due to bioturbation and bio-irrigation (Barnes and Owens, 1998). Usui et al. (1998) calculated the N_2O fluxes from the sediments to range from -0.516 to $-0.156 \text{ } \mu\text{mol N}_2\text{O m}^{-2} \text{ d}^{-1}$ at the continental shelf and from -0.264 to $0.444 \text{ } \mu\text{mol N}_2\text{O m}^{-2} \text{ d}^{-1}$ at the slope region of the East China Sea, the magnitude is lower than benthic

fluxes of N_2O in the Changjiang Estuary and suggests that the Changjiang Estuary can act as a stronger N_2O source or sink than the East China Sea. In summary, this study suggests that sediment can act as either a source or a sink of N_2O in the water column in the Changjiang Estuary.

3.4 Sea-to-air fluxes of N_2O

N_2O saturations in the surface waters of the Changjiang Estuary and its adjacent area ranged from 84% to 363% during the five surveys in this study (Table 1), which showed that the surface waters of studied regions were generally supersaturated with respect to the atmospheric N_2O concentrations all year around except a few stations during November 2002. Hence the Changjiang Estuaries and its adjacent areas represent a net source of N_2O to the atmosphere.

For each station we calculated sea-to-air N_2O flux based on the actual saturation value and the long-term averaged wind speed and the results are summarized in Table 4. From Table 4, it can be seen that the greatest uncertainty for the sea-to-air N_2O flux estimation came from the estimation of gas exchange velocities. Using different relationships yield significantly different transfer velocities under the same wind speed. Generally using LM86 relationship yields a lower value, and using W92 and RC01 relationships lead to relatively higher N_2O flux estimates than using LM86 by a mean factor of about 1.9 and 2.2, respectively. Another important uncertainty in the assessment of the gas transfer velocity and sea-to-air gas fluxes is related to the type of wind data used. Morell et al. (2001) found that fluxes computed using climatological wind speed data often exceed those using ship-based wind speed measurements by over 50%. In this work, we computed the gas transfer velocities for May 2002 and October 2006 using both ship-based in situ wind speed and long-term averaged wind speed. The long-term averaged wind speeds in the studied regions were higher than the mean ship-based in situ wind speeds by 10–130%, hence the obtained N_2O fluxes estimated using long-term wind speed were higher than those using in situ wind speed by 20–280%. The discrepancy between all these sets of flux values suggests that we should pay much attention to the uncertainty involved by using different sea-air exchange models and wind speed data when making comparisons with published data. In this paper only sea-to-air N_2O fluxes estimated using long-term wind speed will be discussed below, hence our results are probably overestimated to some extent.

The sea-to-air N_2O fluxes from the Changjiang Estuary and its adjacent marine area indicated obvious variation with higher values occurring in summer cruise and lower values in spring and autumn cruises (Table 4). The average annual N_2O flux from the Changjiang Estuary and its adjacent marine area was 7.7 ± 5.5 , 15.1 ± 10.8 and $17.0 \pm 12.6 \mu\text{mol m}^{-2} \text{d}^{-1}$ using LM86, W92 and RC01 relationship, respectively. These results are comparable to the flux of $8.4\text{--}12 \mu\text{mol m}^{-2} \text{d}^{-1}$ reported for Tamar estu-

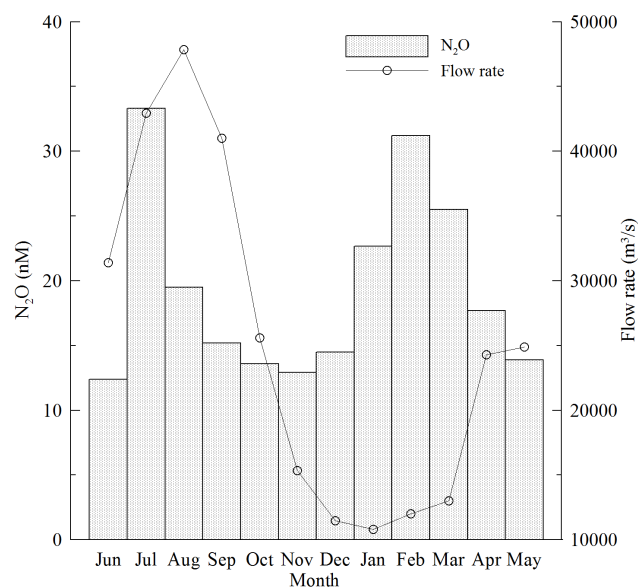


Fig. 6. Monthly variation of N_2O concentrations at Xuliujing and flow rates at Station Datong in the Changjiang from June 2007 to May 2008.

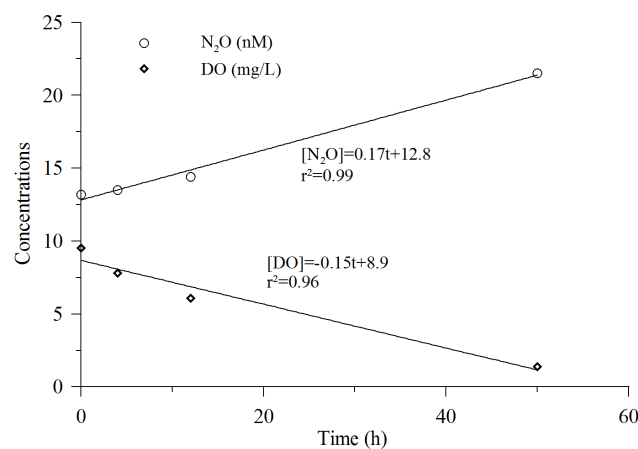


Fig. 7. N_2O (nM) and DO (mg/L) with time during sediment incubation at Station DB6.

ary (Law et al., 1992), but are much lower than the flux of $43\,200 \mu\text{mol m}^{-2} \text{d}^{-1}$ reported for Humber estuary (Barnes and Owens, 1998) and $265.6 \pm 280.4 \mu\text{mol m}^{-2} \text{d}^{-1}$ for Colne estuary (Dong et al., 2004). However, since this study didn't cover the inner estuary and the TMZ of the Changjiang, which is expected to contain high levels of N_2O , flux data in this study may be underestimated to some extent.

The studied area was divided into two areas (i.e. estuary and marine area) according to the salinity of 30. The Changjiang Estuary was mainly limited to $122\text{--}123^\circ \text{E}$ and $29\text{--}32^\circ \text{N}$ and estimated to be $\sim 3.4 \times 10^4 \text{ km}^2$, and its adjacent marine area was limited to the rest area between $122\text{--}125^\circ \text{E}$ and $28\text{--}34^\circ \text{N}$ and estimated to be

Table 4. Sea-to-air N₂O fluxes from the Changjiang Estuary and its adjacent marine area (LM86: K was calculated using the tri-linear k/u_{10} relationship established by Liss and Merlivat (1986); W92: K was calculated using the quadratic k/u_{10} relationship established by Wanninkhof (1992); RC01: K was calculated using the k/u_{10} relationship established by Raymond and Cole (2001).

Seasons	<i>n</i>	Surface N ₂ O (nM)	Surface N ₂ O (%)	ΔC (nM)	<i>U</i> ₁₀ (m/s)	F (LM86) (μmolm ⁻² d ⁻¹)	F (W92) (μmolm ⁻² d ⁻¹)	F (RC01) (μmolm ⁻² d ⁻¹)	Mean Flux (μmolm ⁻² d ⁻¹)
May 2002	24	11.77 ± 2.15	141 ± 23	3.45 ± 1.96	6.7 (5.1 ± 2.0) ^a	6.8 ± 3.8 4.0 ± 4.5	13.2 ± 7.4 7.2 ± 7.1	14.3 ± 8.1 11.2 ± 12.4	11.4 ± 4.1
Nov 2002	27	9.00 ± 2.11	114 ± 25	1.11 ± 2.03	7.6	2.9 ± 5.2	5.8 ± 10.2	6.7 ± 11.8	5.1 ± 2.0
Jun 2006	25	9.10 ± 0.88	119 ± 6	1.45 ± 0.49	6.8	3.1 ± 1.0	6.1 ± 2.0	6.6 ± 2.1	5.3 ± 1.9
Aug 2006	30	10.78 ± 4.25	184 ± 71	4.93 ± 4.22	7.6	16.3 ± 13.8	32.0 ± 27.1	37.0 ± 31.3	28.4 ± 10.7
Oct 2006	29	10.11 ± 1.56	153 ± 24	3.51 ± 1.59	7.2 (5.9 ± 2.7) ^a	9.4 ± 4.3 7.2 ± 7.2	18.4 ± 8.3 12.9 ± 12.2	20.6 ± 9.3 20.7 ± 22.5	16.1 ± 5.9
Annual mean		10.15 ± 1.17	142 ± 28	2.89 ± 1.59	7.2 ± 0.4	7.7 ± 5.5	15.1 ± 10.8	17.0 ± 12.6	13.3 ± 4.9

^a Numbers in the parentheses are the ship-based in situ wind speeds

~16.9 × 10⁴ km². According to the area of Changjiang Estuary and the annual mean atmospheric N₂O flux estimated by RC01 equation which provide reasonable fluxes for estuaries, the annual N₂O emission from the Changjiang Estuary was estimated to be 2.1 × 10⁸ mol yr⁻¹ (equal to 5.8 Gg N yr⁻¹). According to the area of the adjacent marine area and the annual mean atmospheric N₂O flux estimated by W92 equation, the annual N₂O emission from the adjacent marine area was estimated to be 9.3 × 10⁸ mol yr⁻¹ (equal to 25.8 Gg N yr⁻¹). N₂O emission from the Changjiang Estuary accounted for about 0.17% of the total N load (1.85 × 10⁶ t/yr, Zhang et al., 2003) and 0.25% of the DIN load (1.22 × 10⁶ t/yr, Zhang et al., 2003) to the estuary via Changjiang. Considering the inner estuary and the TMZ were not covered in this study, the actual values should be slightly higher. Hence our result is comparable to the conversion ratio of ~0.26% from TN estimated by Robinson et al. (1998) for the Colne estuary and 0.3% from DIN input employed in the global scale models for estuaries (Seitzinger and Kroeze, 1998). N₂O emission from the Changjiang Estuary and its adjacent marine area (31.6 Gg N yr⁻¹) was lower than those from the paddy fields in the Changjiang river basin, but they were of the same order of magnitude. For example, based on the annual N₂O emission from the paddy fields in the Changjiang basin (3.98 Kg N ha⁻¹) and the paddy field area of 16.4 × 10⁶ ha (including the Chengdu Plain, the middle and lower reaches of Yangtze river, the Dongting, Poyang and Taihu Lake plains), N₂O emission from the paddy fields in the main region of the Changjiang basin was estimated to be 65 Gg N yr⁻¹ (Xing, 1998). Hence estuaries (i.e. the Changjiang Estuary), like agricultural land, can act as a significant source of atmospheric N₂O. Since N₂O fluxes may vary greatly in different estuarine systems, more observations at major estuarine systems in the world should be done to understand the estuarine N₂O emissions on a global scale.

4 Conclusions

Dissolved N₂O concentrations in the outer estuary of Changjiang showed great temporal and spatial variations. They fall within but toward the lower end of the N₂O range in the worldwide estuaries, and are consistent with the low DIN levels. Distribution of N₂O in the Changjiang Estuary was influenced by multiple factors and the key factor varied between cruises.

N₂O concentrations in the surface waters of Changjiang showed obvious seasonal variations with higher values occurring in both summer and winter. Annual input of N₂O from the Changjiang to the estuary was estimated to be 15.0 × 10⁶ mol/yr. Sediment can act as either a source or a sink of N₂O in the water column of the Changjiang Estuary. Changjiang Estuary and its adjacent area act as a significant source of atmospheric N₂O. Annual N₂O emissions from the estuary and its adjacent marine area were estimated to be 2.1 × 10⁸ and 9.3 × 10⁸ mol yr⁻¹, respectively. Due to the great spatial variation of N₂O fluxes from different estuaries, more studies on the major estuarine systems in the world are required to estimate the estuarine N₂O emissions accurately on a global scale.

Since external source (i.e. riverine input) only acts as a minor source of N₂O in the Changjiang estuary, in situ production of N₂O in both water column and sediment via nitrification and denitrification is expected to contribute dominantly to the atmospheric N₂O emission from Changjiang estuary. More measurements on N₂O emission rates from sediments and in situ production rates of N₂O in the water column (especially in the estuarine mixing zone and the turbidity maximum zone) at different seasons are required to close the N₂O budget of Changjiang Estuary.

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