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

G.-L. Zhang¹, J. Zhang², S.-M. Liu¹, J.-L. Ren¹, and Y.-C. Zhao¹

¹Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, College of Chemistry and Chemical Engineering, Ocean University of China, 238 Songling Road, 266100 Qingdao, China
²State Key Laboratory of Estuarine and Coastal Research, East China Normal University, 3663 Zhongshan Road North, 200062 Shanghai, China

Received: 22 April 2010 – Published in Biogeosciences Discuss.: 3 May 2010
Revised: 28 October 2010 – Accepted: 2 November 2010 – Published: 9 November 2010

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 × 10⁶ mol/yr. N₂O emission rates from the sediments of the Changjiang Estuary in spring ranged from −1.88 to 2.02 µmol m⁻² 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 ± 12.6 µmol m⁻² 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
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.

The basin covers about 1.8 million km$^2$ in area, which is about one fifth of the total land area of the whole country. The huge amount of runoff discharge (903 km$^3$/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 $\sim 60 \mu$mol/L in the 1980’s to $\sim 80 \mu$mol/L in 1997 (Liu et al., 2003). The DIN flux from the Changjiang has increased from $(0.3 \sim 0.5) \times 10^6$ t/yr in 1970–1980 to $(1.2 \sim 1.5) \times 10^6$ t/yr in late 1990s (Li et al., 2007; Zhang et al., 2003). The dissolved organic nitrogen (DON) and particulate nitrogen (PN) concentrations were $22.5 \pm 19.6$ and $9.1 \pm 4.0 \mu$mol/L at Datong station in the Changjiang, and DON and PN fluxes were estimated to be $0.47 \times 10^6$ and $0.16 \times 10^6$ 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 N$_2$O, the increasing load of nitrogen (DIN, DON and PN) to the Changjiang Estuary may potentially affect the cycling of N$_2$O, its subsequent emission to the atmosphere and to the open sea as well. However, no data are so far available for the distribution, fluxes and production processes of dissolved N$_2$O in the Changjiang Estuary. Hou et al. (2007) studied the N$_2$O production in the intertidal sediments of the Changjiang Estuary, and found that N$_2$O 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 N$_2$O in the outer estuary of the Changjiang and its adjacent marine areas. The objectives of our study were: (1) to determine the distribution of N$_2$O along the Changjiang Estuary; (2) to estimate the N$_2$O emission into the atmosphere; (3) to evaluate the contribution of the Changjiang River to N$_2$O 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 N$_2$O 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 HgCl$_2$ 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$_2$O input to the sea from the Changjiang, N$_2$O concentrations were monitored monthly at Xuliujing (121°2' E, 31°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$_2$O 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 60cm long and 10cm 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$_2$O 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$_2$O/N$_2$ (Research Institute of China National Standard Materials) into the stripper filled with blank seawater. The N$_2$O 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$_2$O analysis in this study was 0.1 nmol/L (MDL is defined as the N$_2$O 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$_2$O 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 SANplus) with precision of <5–10%.

### 2.3 Measurements of sediment-water N$_2$O fluxes

Sediment-water N$_2$O 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$_2$O 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$_2$O concentration to correct the N$_2$O change of the overlying water. The dissolved N$_2$O 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$_2$O fluxes were determined from the slope of the N$_2$O 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$_2$O fluxes ($F$ in mol m$^{-2}$ d$^{-1}$) can be estimated by the following equation

$$F = k \cdot (C_{\text{obs}}-C_{\text{eq}})$$  \hspace{1cm} (1)

Where $C_{\text{obs}}$ is the observed concentration of dissolved N$_2$O; $C_{\text{eq}}$ is the air-equilibrated seawater N$_2$O concentration, which was calculated for in situ temperatures and salinities using the solubility data of Weiss and Price (1980). Atmospheric N$_2$O was not measured during these cruises, and a global mean atmospheric N$_2$O 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 N$_2$O, temperature, salinity and O$_2$ in surface and bottom waters of the Changjiang Estuary and its adjacent area (Numbers in the parentheses are the saturations in %; O$_2$ data for Nov 2002 is not available due to technical troubles).

<table>
<thead>
<tr>
<th>Date</th>
<th>Surface temperature (°C)</th>
<th>Surface salinity</th>
<th>Surface O$_2$ (mg/L)</th>
<th>Surface N$_2$O (nM)</th>
<th>Bottom temperature (°C)</th>
<th>Bottom salinity</th>
<th>Bottom O$_2$ (mg/L)</th>
<th>Bottom N$_2$O (nM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 Apr–3 May 2002</td>
<td>17.4±1.1</td>
<td>28.9±6.6</td>
<td>8.7±0.7</td>
<td>8.17–18.9 (106)</td>
<td>17.5±0.9</td>
<td>31.4±3.3</td>
<td>7.8±1.3</td>
<td>8.49–14.3 (108)</td>
</tr>
<tr>
<td>4–11 Nov 2002</td>
<td>19.4±1.6</td>
<td>27.7±5.3</td>
<td>6.59–16.7</td>
<td>9.00±2.11 (114)</td>
<td>17.5±0.9</td>
<td>30.1±4.6</td>
<td>4.8±11 (119)</td>
<td>5.83–18.2 (125)</td>
</tr>
<tr>
<td>2–11 Jun 2006</td>
<td>20.1±2.2</td>
<td>30.6±2.3</td>
<td>7.48–10.68</td>
<td>9.10±0.88 (119)</td>
<td>18.1±2.3</td>
<td>3.9±1.0</td>
<td>4.9±11 (110)</td>
<td>9.28–16.10 (125)</td>
</tr>
<tr>
<td>15–31 Aug 2006</td>
<td>28.9±0.9</td>
<td>31.2±2.2</td>
<td>6.04–21.32</td>
<td>10.78±4.25 (184)</td>
<td>21.4±3.5</td>
<td>2.4±1.0</td>
<td>3.7±14 (110)</td>
<td>6.67–20.72 (130)</td>
</tr>
<tr>
<td>3–13 Oct 2006</td>
<td>24.5±1.0</td>
<td>32.5±1.5</td>
<td>5.0±0.6</td>
<td>10.11±1.56 (153)</td>
<td>22.5±2.0</td>
<td>3.9±0.8</td>
<td>2.2±14 (125)</td>
<td>6.75–18.44 (134)</td>
</tr>
</tbody>
</table>

3 Results and discussion

3.1 Distributions of N$_2$O in the Changjiang Estuary and its adjacent area

N$_2$O 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 N$_2$O concentrations in the Changjiang Estuary and its adjacent area are shown in Fig. 2. Generally high N$_2$O concentrations were observed beyond the mouth of the Changjiang and Hangzhou Bay, especially in the bottom waters. N$_2$O 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, N$_2$O concentrations in the Changjiang estuary were found to correlate well with salinity in September 2003 ([N$_2$O] = $-0.87 s + 38.2$, $r^2 = 0.79$, $n = 25$, Zhang et al., 2008). This may because that only high salinity area was covered in this study and N$_2$O 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 m$^3$/s) and October 2006 (14 800 m$^3$/s) is 38% and 55% lower than the long-term monthly average water discharge of 44 570 and 35 550 m$^3$/s for August and October. Hence the influence of N-rich freshwater was rather limited in this study. The distributions of N$_2$O 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 N$_2$O production (ΔN$_2$O) 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...
of oxygen is more complicated than expected. The distribution of N\textsubscript{2}O in the Changjiang estuary was also influenced by other environmental factors. For example, N\textsubscript{2}O concentrations correlated with nitrate ([N\textsubscript{2}O] = 0.21[N\textsubscript{NO\textsubscript{3}}] + 8.6, \( n = 120, r^2 = 0.35 \)) and temperature ([N\textsubscript{2}O] = 0.65 t + 26.6, \( n = 120, r^2 = 0.24 \)) in June 2006. N\textsubscript{2}O concentrations in bottom waters correlated well with suspended particulate matter (SPM) ([N\textsubscript{2}O] = 0.01 SPM + 8.0, \( n = 30, r^2 = 0.49 \)) in November 2002. All these results suggest that N\textsubscript{2}O 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 N\textsubscript{2}O 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 N\textsubscript{2}O.

Table 2 shows previously published data on N\textsubscript{2}O in other estuaries, which indicates that N\textsubscript{2}O concentrations vary over a wide range of 2–1457 nM at various temporal and spatial scales. N\textsubscript{2}O 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 N\textsubscript{2}O data in Table 2 covered the full salinity range of 0–30 while N\textsubscript{2}O data in this study were mainly from the high salinity area (salinity of 20–30) of the Changjiang Estuary. High N\textsubscript{2}O 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 N\textsubscript{2}O concentrations in this study only represent the low N\textsubscript{2}O levels in the outer Changjiang Estuary. For example, high concentrations of N\textsubscript{2}O, 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 N\textsubscript{2}O concentrations in the outer Changjiang Estuary in this study were comparable to those reported for the Danube river plume (Amouroux et al., 2002), but lower than those for the Rhone River plume (Marty et al., 2001). On the other hand, N\textsubscript{2}O 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 N\textsubscript{2}O in estuaries are generally found to be related to the estuarine dissolved inorganic nitrogen (DIN) levels (Seitzinger and Kroene, 1998; Dong et al., 2004).
DIN concentrations in the Changjiang estuary in this study were 12.5 ± 5.8, 12.6 ± 8.6 and 15.6 ± 8.0 µM for June, August and October 2006, respectively. Although the correlation between N\textsubscript{2}O concentrations and DIN was not obvious at most cruises, N\textsubscript{2}O and DIN data in the Changjiang Estuary fit well in the plot of estuarine N\textsubscript{2}O versus DIN on a global scale (Fig. 5), suggesting that the low N\textsubscript{2}O observed in this study is consistent with the low DIN levels. In any way, this study highlights the importance of studies on the N\textsubscript{2}O variability of more representative estuaries in the future research to estimate accurately the contribution of estuaries to atmospheric N\textsubscript{2}O.

### 3.2 Riverine input of N\textsubscript{2}O

Figure 6 shows the seasonal variation of dissolved N\textsubscript{2}O 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. N\textsubscript{2}O 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. N\textsubscript{2}O concentrations correlate negatively with the in situ temperature (\([N\textsubscript{2}O]= -0.48t + 27.2, r^2 = 0.45, n = 11, July 2007 is not included\)) while N\textsubscript{2}O saturations showed weak positive correlation with the temperature (\(N\textsubscript{2}O(%) = 5.3t + 109.5, r^2 = 0.21, n = 12\)). This suggest that the high N\textsubscript{2}O concentrations in winter may be partly due to higher N\textsubscript{2}O 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 ± 17.9 µM, among which nitrate is the dominate species with an average of 122.1 ± 17.1 µM and contribute 75%–99% to DIN. N\textsubscript{2}O concentrations correlate positively with DIN (\([N\textsubscript{2}O]= 0.23\text{DIN}-10.6, r^2=0.32, n = 12\)). Table 3 compiled previously published N\textsubscript{2}O concentrations and saturations in various world rivers. It can be seen that N\textsubscript{2}O concentrations in river waters show great spatial and temporal variations with the range from 3.3 to 527 nM. N\textsubscript{2}O concentrations in the surface waters of the Changjiang in this study fall within the reported N\textsubscript{2}O ranges in the worldwide rivers. N\textsubscript{2}O 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 N\textsubscript{2}O production rate of 1.30 ± 0.85 and 346 ± 261 nmol N m\(^{-2}\) h\(^{-1}\) by denitrification in the Changjiang for August and October 2002, respectively. They also observed N\textsubscript{2}O 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 N\textsubscript{2}O 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

### Table 3. Compilation of dissolved N\textsubscript{2}O in various rivers (numbers in the parentheses are the averaged value).

<table>
<thead>
<tr>
<th>Rivers</th>
<th>Description</th>
<th>N\textsubscript{2}O (nM)</th>
<th>N\textsubscript{2}O (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alsea River</td>
<td>Oct 1979</td>
<td>8.2–15.6</td>
<td>94–166</td>
<td>De Angelis and Gordon (1985)</td>
</tr>
<tr>
<td>Arkansas River</td>
<td>Jan/Feb 2000</td>
<td>3.3–5.9 (3.6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>English rivers</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Colne</td>
<td>Aug 2001–May 2002</td>
<td>(44.2 ± 5.0)</td>
<td>(272.5 ± 32.1)</td>
<td>Dong et al. (2004)</td>
</tr>
<tr>
<td>Ouse</td>
<td>Aug 2001–May 2002</td>
<td>(39.2 ± 2.9)</td>
<td>(217.9 ± 16.5)</td>
<td></td>
</tr>
<tr>
<td>Trent</td>
<td>Aug 2001–May 2002</td>
<td>(43.2 ± 3.5)</td>
<td>(228.4 ± 18.3)</td>
<td></td>
</tr>
<tr>
<td>Stour</td>
<td>Aug 2001–May 2002</td>
<td>(53.9 ± 4.5)</td>
<td>(297.4 ± 25.7)</td>
<td></td>
</tr>
<tr>
<td>Orwell</td>
<td>Aug 2001–May 2002</td>
<td>(60.1 ± 5.4)</td>
<td>(389.1 ± 31.7)</td>
<td></td>
</tr>
<tr>
<td>Amazon River</td>
<td>Main stem</td>
<td>(13.4 ± 2.5)</td>
<td></td>
<td>Richey et al. (1988)</td>
</tr>
<tr>
<td>Changjiang</td>
<td>Aug 2002</td>
<td>9.02 ± 1.03</td>
<td></td>
<td>Yan et al. (2004)</td>
</tr>
<tr>
<td></td>
<td>Oct 2002</td>
<td>13.39 ± 8.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Jan 2008</td>
<td>22.0 ± 3.5</td>
<td>168 ± 27</td>
<td>Zhao et al. (2009)</td>
</tr>
<tr>
<td></td>
<td>Jun 2007–May 2008</td>
<td>19.4 ± 7.3</td>
<td>213 ± 97</td>
<td>This study</td>
</tr>
<tr>
<td>Pearl River</td>
<td>Sep 2003</td>
<td>20–40</td>
<td></td>
<td>Chen et al. (2008)</td>
</tr>
<tr>
<td></td>
<td>Apr 2004</td>
<td>62–323 (143)</td>
<td>720–4080 (1730)</td>
<td>Xu et al. (2005)</td>
</tr>
</tbody>
</table>
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\textsubscript{2}O from the Changjiang to the estuary by multiplying the monthly river water N\textsubscript{2}O concentration by the monthly flow rate, which yields a N\textsubscript{2}O flux of 0.5 mol/s equal to 15.0 × 10\textsuperscript{6} mol/yr for the annual input. N\textsubscript{2}O input via Changjiang contributes about 7% to the N\textsubscript{2}O emission from the estuary (see below), and is a minor source for dissolved N\textsubscript{2}O in the Changjiang Estuary.

\subsection*{3.3 Sediment-water N\textsubscript{2}O fluxes}

In estuarine and coastal regions, the sediments are likely to be important sources of N\textsubscript{2}O 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\textsubscript{2}O 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\textsubscript{2}O 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\textsubscript{2}O 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\textsubscript{2}O together with the decrease of O\textsubscript{2} in the overlying water was observed.
during sediment incubation at station DB6 (Fig. 7). Sediment oxygen consumption rates and N\textsubscript{2}O effluxes from the sediments were calculated to be 32.9 mmol m\textsuperscript{-2} d\textsuperscript{-1} and 2.02 µmol m\textsuperscript{-2} d\textsuperscript{-1}, respectively. Incubation experiments of nutrient exchange between sediment-water interface under oxic environments showed that nitrate and NH\textsubscript{4}\+ was transferred from the water column to sediment (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, O\textsubscript{2} is not easily transferred to the sediment. These suggest that N\textsubscript{2}O can be produced via both nitrification and denitrification in the sediment at station DC10, but the occurrence of N\textsubscript{2}O reduction simultaneously with the production by denitrification induced net consumption of N\textsubscript{2}O in the sediment. Li et al. (2009) reported that the sediment denitrification rates ranged from 101.3 to 731.9 µmol N\textsubscript{2}O m\textsuperscript{-2} h\textsuperscript{-1} in June 2006 in the Changjiang Estuary. Previous studies showed that benthic N\textsubscript{2}O fluxes from sediments showed highly temporal and spatial variations (−5 to 600 µmol N\textsubscript{2}O m\textsuperscript{-2} d\textsuperscript{-1}; Kieskamp et al., 1991; Barnes and Owens, 1998; Usui et al., 1998; Laursen and Seitzinger, 2002). Benthic N\textsubscript{2}O fluxes obtained in this study fell within the general range, and were consistent with those reported for Mid-Atlantic bight (−1.82–2.03 µmol N\textsubscript{2}O m\textsuperscript{-2} d\textsuperscript{-1}), which also showed highly variable in both magnitude and direction of N\textsubscript{2}O 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 (1.2–102 µmol N\textsubscript{2}O m\textsuperscript{-2} d\textsuperscript{-1}). High N\textsubscript{2}O 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\textsubscript{2}O fluxes from the sediments to range from −0.516 to −0.156 µmol N\textsubscript{2}O m\textsuperscript{-2} d\textsuperscript{-1} at the continental shelf and from −0.264 to 0.444 µmol N\textsubscript{2}O m\textsuperscript{-2} d\textsuperscript{-1} at the slope region of the East China Sea, the magnitude is lower than benthic
fluxes of N\textsubscript{2}O in the Changjiang Estuary and suggests that the Changjiang Estuary can act as a stronger N\textsubscript{2}O 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\textsubscript{2}O in the water column in the Changjiang Estuary.

3.4 Sea-to-air fluxes of N\textsubscript{2}O

N\textsubscript{2}O 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\textsubscript{2}O 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\textsubscript{2}O to the atmosphere.

For each station we calculated sea-to-air N\textsubscript{2}O 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\textsubscript{2}O 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\textsubscript{2}O 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\textsubscript{2}O 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\textsubscript{2}O 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\textsubscript{2}O 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\textsubscript{2}O flux from the Changjiang Estuary and its adjacent marine area was 7.7 ± 5.5, 15.1 ± 10.8 and 17.0 ± 12.6 µmol m\textsuperscript{-2} d\textsuperscript{-1} using LM86, W92 and RC01 relationship, respectively. These results are comparable to the flux of 8.4–12 µmol m\textsuperscript{-2} d\textsuperscript{-1} reported for Tamar estuary (Law et al., 1992), but are much lower than the flux of 43 200 µmol m\textsuperscript{-2} d\textsuperscript{-1} reported for Humber estuary (Barnes and Owens, 1998) and 265.6 ± 280.4 µmol m\textsuperscript{-2} d\textsuperscript{-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\textsubscript{2}O, 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 122–123° E and 29–32° N and estimated to be ∼3.4 × 10\textsuperscript{4} km\textsuperscript{2}, and its adjacent marine area was limited to the rest area between 122–125° E and 28–34° N and estimated to be

![Fig. 6. Monthly variation of N\textsubscript{2}O concentrations at Xuliujing and flow rates at Station Datong in the Changjiang from June 2007 to May 2008.](image)

![Fig. 7. N\textsubscript{2}O (n M) and DO (mg/L) with time during sediment incubation at Station DB6.](image)
Table 4. Sea-to-air N$_2$O 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).

<table>
<thead>
<tr>
<th>Seasons</th>
<th>n</th>
<th>Surface N$_2$O (nM)</th>
<th>Surface N$_2$O (%)</th>
<th>$\Delta$C (nM)</th>
<th>$U_{10}$ (m/s)</th>
<th>F (LM86) (µmol m$^{-2}$ d$^{-1}$)</th>
<th>F (W92) (µmol m$^{-2}$ d$^{-1}$)</th>
<th>F (RC01) (µmol m$^{-2}$ d$^{-1}$)</th>
<th>Mean Flux (µmol m$^{-2}$ d$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>May 2002</td>
<td>24</td>
<td>11.77 ± 2.15</td>
<td>141 ± 23</td>
<td>3.45 ± 1.96</td>
<td>6.7</td>
<td>6.8 ± 3.8</td>
<td>13.2 ± 7.4</td>
<td>14.3 ± 8.1</td>
<td>11.4 ± 4.1</td>
</tr>
<tr>
<td>Nov 2002</td>
<td>27</td>
<td>9.00 ± 2.11</td>
<td>114 ± 25</td>
<td>1.11 ± 2.03</td>
<td>7.6</td>
<td>4.0 ± 4.5</td>
<td>7.2 ± 7.1</td>
<td>11.2 ± 12.4</td>
<td>5.1 ± 2.0</td>
</tr>
<tr>
<td>Jun 2006</td>
<td>25</td>
<td>9.10 ± 0.88</td>
<td>119 ± 6</td>
<td>1.45 ± 0.49</td>
<td>6.8</td>
<td>2.9 ± 5.2</td>
<td>5.8 ± 10.2</td>
<td>6.7 ± 11.8</td>
<td>5.1 ± 2.0</td>
</tr>
<tr>
<td>Aug 2006</td>
<td>30</td>
<td>10.78 ± 4.25</td>
<td>184 ± 71</td>
<td>4.93 ± 4.22</td>
<td>7.6</td>
<td>3.1 ± 1.0</td>
<td>6.1 ± 2.1</td>
<td>6.6 ± 2.1</td>
<td>5.3 ± 1.9</td>
</tr>
<tr>
<td>Oct 2006</td>
<td>29</td>
<td>10.11 ± 1.56</td>
<td>153 ± 24</td>
<td>3.51 ± 1.59</td>
<td>7.2</td>
<td>9.4 ± 4.3</td>
<td>18.4 ± 8.3</td>
<td>20.6 ± 9.3</td>
<td>16.1 ± 5.9</td>
</tr>
<tr>
<td>Annual mean</td>
<td>29</td>
<td>10.15 ± 1.17</td>
<td>142 ± 28</td>
<td>2.89 ± 1.59</td>
<td>7.2 ± 0.4</td>
<td>7.7 ± 5.5</td>
<td>15.1 ± 10.8</td>
<td>17.0 ± 12.6</td>
<td>13.3 ± 4.9</td>
</tr>
</tbody>
</table>

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

$\sim 16.9 \times 10^4$ km$^2$. According to the area of Changjiang Estuary and the annual mean atmospheric N$_2$O flux estimated by RC01 equation which provide reasonable fluxes for estuaries, the annual N$_2$O emission from the Changjiang Estuary was estimated to be $2.1 \times 10^8$ 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 N$_2$O flux estimated by W92 equation, the annual N$_2$O emission from the adjacent marine area was estimated to be $9.3 \times 10^8$ mol yr$^{-1}$ (equal to 25.8 Gg N yr$^{-1}$). N$_2$O emission from the Changjiang Estuary accounted for about 0.17% of the total N load ($1.85 \times 10^8$ t/yr, Zhang et al., 2003) and 0.25% of the DIN load ($1.22 \times 10^8$ 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 $\sim 0.26$% 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). N$_2$O 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 N$_2$O emission from the paddy fields in the Changjiang basin ($3.98$ Kg N ha$^{-1}$) and the paddy field area of $16.4 \times 10^6$ ha (including the Chengdu Plain, the middle and lower reaches of Yangtze river, the Dongting, Poyang and Taihu Lake plains), N$_2$O 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 N$_2$O. Since N$_2$O fluxes may vary greatly in different estuarine systems, more observations at major estuarine systems in the world should be done to understand the estuarine N$_2$O emissions on a global scale.

4 Conclusions

Dissolved N$_2$O concentrations in the outer estuary of Changjiang showed great temporal and spatial variations. They fall within but toward the lower end of the N$_2$O range in the worldwide estuaries, and are consistent with the low DIN levels. Distribution of N$_2$O in the Changjiang Estuary was influenced by multiple factors and the key factor varied between cruises.

N$_2$O concentrations in the surface waters of Changjiang showed obvious seasonal variations with higher values occurring in both summer and winter. Annual input of N$_2$O from the Changjiang to the estuary was estimated to be $15.0 \times 10^8$ mol yr$^{-1}$. Sediment can act as either a source or a sink of N$_2$O in the water column of the Changjiang Estuary. Changjiang Estuary and its adjacent area act as a significant source of atmospheric N$_2$O. Annual N$_2$O emissions from the estuary and its adjacent marine area were estimated to be $2.1 \times 10^8$ and $9.3 \times 10^8$ mol yr$^{-1}$, respectively. Due to the great spatial variation of N$_2$O fluxes from different estuaries, more studies on the major estuarine systems in the world are required to estimate the estuarine N$_2$O emissions accurately on a global scale.

Since external source (i.e. riverine input) only acts as a minor source of N$_2$O in the Changjiang estuary, in situ production of N$_2$O in both water column and sediment via nitrification and denitrification is expected to contribute dominantly to the atmospheric N$_2$O emission from Changjiang estuary. More measurements on N$_2$O emission rates from sediments and in situ production rates of N$_2$O in the water column (especially in the estuarine mixing zone and the turbidity maximum zone) at different seasons are required to close the N$_2$O budget of Changjiang Estuary.

Acknowledgements. The authors wish to thank the crew of the R/V “Haitjian 47”, R/V “Science No. 1”, R/V “Haitijian 49” and R/V “Beidou” and colleagues from the Laboratory of Marine Biogeochemistry, Ocean University of China for assistances in field sample collections. D. J. Huang and W. J. Jian are acknowledged for providing us with the hydrographic and climatologic data. This

Biogeosciences, 7, 3505–3516, 2010 www.biogeosciences.net/7/3505/2010/
study was funded by the Ministry of Science and Technology of China through grant No. 2006CB400601, and by National Science Foundation of China through grant Nos. 41076067, 40876054 and 40925017.

Edited by: J. Middelburg

References


Seitzinger, S. P. and Kroeze, C.: Global distribution of nitrous oxide production and N inputs in freshwater and coastal marine ecosys-