Effect of dissolved oxygen and nitrogen on emission of N\textsubscript{2}O from rivers in China

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**ABSTRACT**

Six rivers from three watersheds in China were chosen to study the temporal and spatial variations in nitrous oxide (N\textsubscript{2}O) concentrations and emissions in order to examine the link between N\textsubscript{2}O production and dissolved oxygen (DO) and nitrogen levels. These rivers can generally be divided into two types: runoff rivers with significant natural and agricultural runoff, and urban rivers with significant urban effluents. The results showed that N\textsubscript{2}O concentrations were 0.15–1.07 (mean 0.51) and 0.22–22.7 (mean 4.10)\,\textmu g\,N\,L\textsuperscript{-1} in runoff rivers and an urban river, respectively. N\textsubscript{2}O was oversaturated in almost all the rivers, suggesting that the rivers were sources of atmospheric N\textsubscript{2}O. N\textsubscript{2}O emissions in the urban river (range from 1.53 to 2453, mean 529\,\textmu g\,N\,m\textsuperscript{-2}\,h\textsuperscript{-1}) were significantly higher than those in runoff rivers (range from 0.51 to 80.9, mean 18.0\,\textmu g\,N\,m\textsuperscript{-2}\,h\textsuperscript{-1}). We found a significant positive correlation of N\textsubscript{2}O production with NO\textsubscript{3} (\textit{r}^2 = 0.30, p < 0.001) and a negative correlation of N\textsubscript{2}O production with DO concentrations (\textit{r}^2 = 0.22, p < 0.001) in runoff rivers. Particularly, there existed a significant positive relationship (\textit{r}^2 = 0.21, p < 0.001) between NH\textsubscript{4} and N\textsubscript{2}O production in an urban river. By using stepwise regression analysis, we found N\textsubscript{2}O production can be predicted by the dynamics of DO and N levels: for runoff rivers, NO\textsubscript{3} and DO explained 47% variability in N\textsubscript{2}O production, while for the urban river, NH\textsubscript{4} and DO explained 64% variability in N\textsubscript{2}O production. We suggest that the IPCC method to calculate N\textsubscript{2}O emission factors should be revised in view of the importance of these multiple factors.

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1. Introduction

Nitrous oxide (N\textsubscript{2}O) is one of the most important greenhouse gases contributing to climate change and is a major ozone depleting substance. Human perturbation of the global nitrogen (N) cycle has increased N\textsubscript{2}O emissions from terrestrial and aquatic ecosystems, and increased atmospheric N\textsubscript{2}O (Seitzinger, 1988; Bouwman, 1996; Ivens et al., 2011). Rivers are a vital sink for terrestrial N considering that 20–25% of anthropogenic N added to the biosphere is exported from rivers to the ocean and inland basins (Howarth et al., 1996; Boyer et al., 2006; Yan et al., 2010). Previous studies have demonstrated that N\textsubscript{2}O production and emission from diverse rivers respond significantly to increasing anthropogenic N loading (Cole and Caraco, 2001;
Numerous investigations have reported strong correlations between dissolved N2O and NO3 concentration in river waters (Herrman et al., 2008; Silvennoinen et al., 2008). Yan et al. (2012) concluded that NO3 is a valid predictor of river N2O production in a large-deep river. However, some studies have failed to find the relationship in river waters. For example, Clough et al. (2006) suggested degassing of the antecedent N2O occurred without any concurrent transformation of the NO3 in a spring fed river where no significant relationship between NO3 and N2O was found. Rosamond et al. (2012) reported that N2O was largely produced by denitrification in hypoxic or anoxic sediment in the Grand River where widespread hypoxia rather than increasing N exports may lead to increased N2O emission. In contrast to NO3, several investigators have demonstrated a negative correlation between DO and dissolved N2O (Yoshinari, 1976; Zhan and Chen, 2006; Rosamond et al., 2011, 2012).

To facilitate estimation of N2O emissions from aquatic systems (streams, rivers, and estuaries), the Intergovernmental Panel on Climate Change (IPCC) methodology has recommended an emission factor (EF5-r). The value (0.75%) that was initially proposed for that factor was obtained from a few riverine systems and was recognized to have a high degree of uncertainty (Nevison, 2000). The EF5-r value was later revised to 0.25% (IPCC, 2006) based on new data from different world regions (Reay et al., 2005; Sawamoto et al., 2005). However, the validity of the emission factor still remains uncertain. For example, a recent study (Beaulieu et al., 2011) showed that globally, more than 0.68 Tg yr−1 of anthropogenic N inputs were converted to N2O in river networks. This value was three times greater than that estimated using IPCC methodology. On the other hand, some studies reported that NO3 concentrations did not limit river N2O production (Clough et al., 2006; Rosamond et al., 2012). Therefore, quantifying riverine N2O emissions is relatively complex and uncertain.

As a result of rapid economic development, many rivers across China are subjected to unprecedented N pollution. Specific factors leading to increased N pollution include: increased N runoff from agricultural fields and livestock as well as urban effluents (Yan et al., 2010; Chen and Hong, 2011). As N inputs to rivers markedly increase, there is the potential for significant increases in N2O production in river systems (Seitzinger, 1988; Bouwman, 1996), and riverine N2O emission from China has a measurable impact on...
global N\textsubscript{2}O emission from aquatic systems (Seitzinger and Kroeze, 1998). Thus far, most reports have focused on N\textsubscript{2}O emissions from lakes, reservoirs and estuaries in China (Wang et al., 2007, 2009; Zhang et al., 2010; Liu et al., 2011; Yang et al., 2012), and direct measurement of riverine N\textsubscript{2}O production and emission in Chinese watersheds has been limited (Yan et al., 2004; Yang et al., 2011; Yu et al., 2013).

Here we report on N\textsubscript{2}O production and emission from 6 rivers across three watersheds in south-central China. The objectives were to: 1) investigate the spatial and temporal (seasonal and diurnal) variations in dissolved N\textsubscript{2}O concentrations from diverse rivers; 2) investigate the links between N\textsubscript{2}O production, DO and inorganic N levels in river systems, and 3) build N\textsubscript{2}O predictive models for various kinds of rivers based on the relationship between N\textsubscript{2}O production, DO and inorganic N levels among the study rivers.

2. Materials and methods

2.1. Study area

The study was conducted in three watersheds in China, the Changjiang River basin, the Chaohu Lake watershed, and the Jiulong River watershed (Fig. 1). The Changjiang River is the third largest river (6.4 x 10\textsuperscript{9} km\textsuperscript{3}) in the world, with an average annual discharge of 10 x 10\textsuperscript{11} m\textsuperscript{3}. The basin (24.27°–35.54°N, 90.13°–122.19°E) covers an area of 1.8 x 10\textsuperscript{6} km\textsuperscript{2}. The average annual temperature is 16–18 °C, and the average rainfall is 1.1 x 10\textsuperscript{3} mm/yr. Datong hydrological station (DHS), at the upstream limit of the estuary, is free from the influence of both tidal cycles and industrial waste from nearby cities. The stretch of the Changjiang River above DHS drains 94% of the total catchment and delivers more than 95% of the water to the estuary (Yan et al., 2003). The Chaohu Lake watershed (116°24′–118°00′E, 30°58′–32°58′N), with a catchment area of 1.3 x 10\textsuperscript{4} km\textsuperscript{2}, is located in the downstream Changjiang River basin (Fig. 1). The watershed bears the strongest impact of human activities in nearby cities. The Nanfei River and the Hangbu River are two large tributaries of the Chaohu Lake system: the Nanfei River is an urban river (urban effluents >70%) with an average discharge of 1.5 x 10\textsuperscript{3} m\textsuperscript{3}/yr, while the Hangbu River receives significant inputs from agricultural runoff (>80%), and has an average discharge of 19.3 x 10\textsuperscript{3} m\textsuperscript{3}/yr. The Jiulong River watershed (116°47′–118°02′E, 24°24′–25°53′N), with a catchment area of 1.47 x 10\textsuperscript{4} km\textsuperscript{2}, is located in southeastern China. The Jiulong River discharges about 12.4 x 10\textsuperscript{8} m\textsuperscript{3}/yr of water via an estuary into Xiamen Bay and then to the southwestern Taiwan Strait. The average annual temperature and rainfall of the watershed are 21 °C and 1.6 x 10\textsuperscript{11} mm/yr, respectively. There are two large tributaries, North River and West Jiulong River, and the Zhuxi Stream is a second order stream in the mid North Jiulong River. All three rivers/streams are subject to significant N inputs from agricultural runoff (>60%). Characteristics of the studied rivers are detailed in Table 1.

2.2. Field sampling

A total of 13 sites were chosen to take samples in 6 rivers located in the three watersheds (Fig. 1 and Table 1). Detailed sampling information is provided below. In the Changjiang River basin, samples were taken for spatial, seasonal and diurnal study, respectively. To investigate spatial variations, samples were taken in October and November 2011 at six national hydrological stations (A1, A4, A5, A6, A7 and A8). Seasonal variations were studied at three sites (A1, A2, and A3). Monthly samples were taken from the three sites from June to December 2009. For diurnal variation research, samples from site A1 were collected on two occasions (August 20–22 and October 26–28, 2009). Samples were collected at 6 h intervals for a period of 60 consecutive hours. In the Chaohu Lake watershed, one site in each river (B1 in the Nanfei River, B2 in the Hangbu River) was sampled monthly in 2006 and 2009. In the Jiulong River watershed, two sites in the two main tributaries (C1 in the North Jiulong River, C2 in the West Jiulong River), and one site (C3) in the outlet of the Zhuxi Stream were selected for monthly sampling from January through December 2010.

On each sampling occasion, surface (~0.5 m) water samples were collected, and water flow rate, water and air temperature, wind speed, and DO were measured in-situ. Samples for NO\textsubscript{2}O analysis were collected by filling 60-ml glass serum bottles from the sampler. Samples were preserved by adding a small crystal of KOH to each bottle immediately before sealing (Yan et al., 2012). All samples were collected in triplicate. An additional surface water sample was collected in a 200-ml glass bottle to determine the NO\textsubscript{3} and NH\textsubscript{4} concentrations. Water temperature and DO were measured using a portable meter (YSI 550A). DO concentrations were calibrated using an iodometric method in the lab.

Table 1

| Study rivers\textsuperscript{a} | Catchment area (km\textsuperscript{2}) | Sampling sites\textsuperscript{b} | Location | River length (km) | River width (m) | River depth (m) | DIN (mg/L) | Dominant land use (%)\textsuperscript{c} |
|-----------------------------|---------------------------------|-------------------------------|----------|-----------------|----------------|---------------|-----------|-----------------------------------|
| CR                          | 1,710,000                       | A1                            | 117°18′ 30′56″ | 5776            | 1540           | 15            | 1.45      | 0.05 Forest (>60)                   |
|                            |                                 | A2                            | 118°28′ 31′43″ | 5926            | 1780           | 15            | 1.74      | 0.05 Forest (>60)                   |
|                            |                                 | A3                            | 117°02′ 30′31″ | 5650            | 1310           | 14            | 0.86      | 0.30                              |
|                            | 1,333,200                       | A4                            | 114°04′ 30′38″ | 5264            | 980            | 24            | 1.94      | 0.17 Forest (>60)                   |
|                            |                                 | A5                            | 108°25′ 30′45″ | 4226            | 750            | 90            | 1.56      | 0.06                              |
|                            | 866,560                        | A6                            | 106°36′ 29′17″ | 3905            | 760            | 20            | 1.49      | 0.05 Forest (>60)                   |
|                            | 159,000                        | A7                            | 111°29′ 28′54″ | 1570            | 270            | 53            | 3.09      | 0.14 Forest (>60)                   |
|                            | 160,200                        | A8                            | 106°25′ 29′51″ | 1119            | 172            | 26            | 1.75      | 0.11 Forest (>60)                   |
| NFR                        | 1618                           | B1                            | 117°22′ 31′49″ | 85              | 170            | 3.0           | 0.514     | 12.54 Urban (>70)                  |
| HBR                        | 2070                           | B2                            | 117°16′ 31′31″ | 139             | 120            | 2.0           | 0.732     | 0.274 Agro (>80)                   |
| NJR                        | 9554                           | C1                            | 117°47′ 117°31′ | 226             | 420            | 7.0           | 2.38      | 0.451 Forest (69)                  |
| WJR                        | 3772                           | C2                            | 117°31′ 117°35′ | 60              | 210            | 2.5           | 2.02      | 0.317 Forest (77)                  |
| ZXS                        | 142                            | C3                            | 117°36′ 117°43′ | 10              | 40             | 0.5           | 3.45      | 0.297 Forest (66)                  |

\textsuperscript{a} Changjiang River (CR); Nanfei River (NFR); Hangbu River (HBR); Zhuxi Stream (ZXS); North Jiulong River (NJR); West Jiulong River (WJR).

\textsuperscript{b} Datong hydrological station (A1); Maanshan hydrological station (A2); Anqing hydrological station (A3); Hankou hydrological station (A4); Wanzhou hydrological station (A5); Cuntan hydrological station (A6); Xiantao hydrological station (A7); Beibei hydrological station (A8); Xingang (B1); Datanwan (B2); Jiangdong station (C1); Zhendian station (C2); Zhuxi station (C3).

\textsuperscript{c} Data from Yan et al., 2010, 2012; Yang et al., 2011.
2.3. Analytical methods

Dissolved N\(_2\)O concentrations were measured using GC-ECD on a Shimadzu GC-2014 gas chromatograph following the headspace-equilibrium method (Huttunen et al., 2002; Walter et al., 2006; Clough et al., 2007). Specifically, 10-mL of highly purified N\(_2\) (purity > 99.999%) was injected into the sampling bottle using an airtight syringe and a 10-mL water sample was displaced. The bottles were then shaken vigorously for 10 min and equilibrated for 4 h. 5-mL of the headspace gas was drawn out and injected into a gas chromatograph (GC-2014, Shimadzu, Japan).

N\(_2\)O concentration was determined using a GC-ECD, two Poropak Q columns for analysis and back flush, and a 1-mL sample loop. The concentrations were standardized using a series of certified standards (100, 500, 1000, 10,000 and 50,000 ppbv; Matheson tri-Gas, Praxair). System precision was less than 1% relative standard deviation.

Initial N\(_2\)O concentrations (\(C_w\)) in water samples were determined using the method described in Johnson et al. (1990). Filtered water samples were analyzed for NH\(_3\) using the phenol-hypochlorite method, and for nitrate using the UV spectrophotometric method (China EPA, 2002). Measurement precision for nutrient components was estimated by repeated determinations of 10% of the samples, and was better than 5%.

2.4. Calculation

Water N\(_2\)O saturation was calculated by the following equation,

\[
\text{N}_2\text{O} \text{ saturation} = \frac{[\text{N}_2\text{O}_\text{meas}]}{[\text{N}_2\text{O}_\text{equ}]} \times 100\% \tag{1}
\]

Where, \([\text{N}_2\text{O}_\text{meas}]\) is the measured N\(_2\)O concentration (\(\mu\)g N L\(^{-1}\)), and \([\text{N}_2\text{O}_\text{equ}]\) is the equilibrium N\(_2\)O concentration of river water with the atmosphere (\(\mu\)g N L\(^{-1}\)), which was calculated using Henry’s Law (Lide and Fredrikse, 1995).

The excess N\(_2\)O (\(\Delta[N_2O], \mu\)g N L\(^{-1}\)) is defined as the difference between \([\text{N}_2\text{O}_\text{meas}]\) and \([\text{N}_2\text{O}_\text{equ}]\).

\[
\Delta[N_2O] = [\text{N}_2\text{O}_\text{meas}] - [\text{N}_2\text{O}_\text{equ}] \tag{2}
\]

Water surface emissions of N\(_2\)O were calculated based on the gas transfer velocity and \(\Delta[N_2O] \) (Raymond and Cole, 2001; Garnier et al., 2006):

\[
F = \Delta[N_2O] \times k_{N2O} \tag{3}
\]

Where, \(F\) is the water surface emissions of N\(_2\)O (\(\mu\)g N m\(^{-2}\) h\(^{-1}\)), and \(k_{N2O}\) (cm h\(^{-1}\)) is the gas transfer velocity.

\(k_{N2O}\) was calculated by the following equation (Wanninkhof, 1992):

\[
k_{N2O} = k_{600} \times \left(\frac{S_{N2O}}{600}\right)^n \tag{4}
\]

Where, \(S_{N2O}\) is the Schmidt number for N\(_2\)O and was calculated according to Wanninkhof (1992) at the in situ temperature, and \(n\) is the Schmidt number coefficient (2/3 for smooth surfaces, decreasing to 1/2 in the presence of breaking waves). \(k_{600}\) will vary due to differences in the physical controls on water turbulence across the studied rivers. Turbulence in surface waters is a balance between wind and water currents that is determined by a variety of factors (e.g., bottom friction, current velocity) (MacIntyre and Melack, 1995). Raymond and Cole (2001) found that \(k\) scales with the product of water current velocity and slope in small rivers and streams, while Alin et al. (2011) found wind dominance in large rivers. In our study, \(k_{600}\) was significantly related to wind speed at 10 m height (\(u_{10}\)) for those rivers with a water flow rate lower than 0.5 m s\(^{-1}\), we used the method of Rasera et al. (2013) to estimate \(k_{600}\) by equation (5).

\[
k_{600} = 3.3(\pm1.6) + 4.2(\pm0.6) \times u_{10} \tag{5}
\]

For rivers with a water flow rate higher than 0.5 m s\(^{-1}\), we used the method of Borges et al. (2004) to estimate \(k_{600}\) by equation (6), accounting for both wind speed and water flow rate:

\[
k_{600} = 1.0 + 1.719(w/h)^{0.5} + 2.58u_{10} \tag{6}
\]

Where is the water flow rate (m s\(^{-1}\)) and \(h\) is the depth of the river water column (m).

To compare gas transfer velocity values among studied rivers, the uncertainty in estimates of \(k_{600}\) values by equations (5) and (6) were discussed (Table 2). There was no significant difference (ANOVA, \(a = 0.05, p = 0.232\)) of \(k_{600}\) values by equations (5) and (6) for those rivers with a water flow rate lower than 0.5 m s\(^{-1}\) (Nanf£i River, Hangbu River, Zhuxi Stream, North Jiulong River and West Jiulong River). However, \(k_{600}\) by equation (5) was 4–27% higher than by equation (6) among those rivers with a water flow rate higher than 0.5 m s\(^{-1}\) (Changjiang River). The effect of this uncertainty on N\(_2\)O emissions is discussed in section 4.3.

We calculated the river N\(_2\)O emission factor (\(EF5-r\), IPCC, 2006) to compare to IPCC predictions based on NO\(_3\). \(EF5-r\) is calculated as:

\[
EF5 - r = \frac{[N_2O - N]/[NO_3^3 - N]}{100} \tag{7}
\]

where, \(EF5-r\) is the river N\(_2\)O emission factor (%), \([N_2O - N]\) is the dissolved N\(_2\)O concentration (\(\mu\)g N L\(^{-1}\)), and \([NO_3^3 - N]\) is the water NO\(_3\) concentration (\(\mu\)g N L\(^{-1}\)).

Apparent oxygen utilization (AOU, mg L\(^{-1}\)) is defined as the difference between the measured oxygen content and the
saturation oxygen content of river water (Yoshinari, 1976; Cohen and Gordon, 1979), as shown in equation (8).

\[
AOU = [DO_{sat}] - [DO_{meas}]
\]

(8)

Where, \([DO_{sat}]\) is the DO saturation concentration (mg L\(^{-1}\)) and \([DO_{meas}]\) is the measured DO concentration (mg L\(^{-1}\)).

SPSS 17.0 statistics software (SPSS Inc.) was used for modeling and data analysis. Pearson correlation analysis was applied to analyze relationships between \(\Delta N_2O\), DO, NO\(_3\), DIN, AOU and water temperature. Spatial differences in N\(_2\)O, DO, \(\Delta N_2O\) and N\(_2\)O emissions were analyzed using one-way ANOVA (\(\alpha = 0.05\)). Regression analysis between N\(_2\)O production and river chemistry factors was carried out using stepwise linear regression, with significance testing by ANOVA.

3. Results

3.1. River chemistry and N\(_2\)O concentrations

DO concentrations varied widely across the sampled sites,
ranging from 0.02 to 11.3 mg L\(^{-1}\). The lowest DO concentration was observed in an urban river (Nanfei River, 1.56 ± 1.01 mg L\(^{-1}\)), while the highest value was observed in the Changjiang River (average 8.19 ± 1.01 mg L\(^{-1}\)) (Fig. 2a). DO concentrations were negatively related to water temperatures in the Changjiang River (\(r^2 = 0.88\), \(P < 0.001\)).

Similar to the patterns of DO concentrations, NO\(_3\), NH\(_4\)+ and DIN (NO\(_3\) + NH\(_4\)+) concentrations showed marked spatial and temporal variations (Fig. 2b–c). However, DIN composition in the Nanfei River was different to other rivers as it was dominated by the NH\(_4\)+–N fraction, which represented more than 90% of DIN on average. In all other rivers, DIN was dominated by the NO\(_3\)–N fraction, which represented 60% of the DIN fraction on average.

N\(_2\)O concentrations ranged from 0.15 to 22.7 μg N L\(^{-1}\). The highest N\(_2\)O concentrations were observed in the Nanfei River and the lowest N\(_2\)O concentrations were found in the Hangbu River during 2006–2009 (Fig. 2d). Most of rivers/streams were most super saturated with N\(_2\)O (90–8213% saturation) during the sampling period. Compared to reports for other rivers around the world (Table 3), the N\(_2\)O super-saturations were typically low in the Changjiang River, but extremely high (more than 100%) in the Nanfei River. Over the two 60-h periods in August and October, N\(_2\)O concentrations ranged from 0.26 to 0.34 ug N L\(^{-1}\) (saturations ranged from 154% to 198%) and from 0.44 to 0.52 ug N L\(^{-1}\) (saturations ranged from 209% to 235%), respectively. During daytime (10:00–16:00), N\(_2\)O concentrations varied from 0.26 to 0.31 ug N L\(^{-1}\) in August and from 0.44 to 0.50 ug N L\(^{-1}\) in October. At night (22:00–4:00), N\(_2\)O concentrations varied from 0.28 to 0.34 ug N L\(^{-1}\) in August and from 0.45 to 0.52 ug N L\(^{-1}\) in October. We found that there were no significant differences (one-way ANOVA test, \(p > 0.05\)) in diurnal patterns (day vs. night) of N\(_2\)O concentrations and saturations over a consecutive 60-h period in each observation in the Changjiang River. On the other hand, N\(_2\)O concentrations ranged from 0.64 to 0.81 ug N L\(^{-1}\) with an average of 0.72 ± 0.05 ug N L\(^{-1}\) across all locations sampled (A1, A4, A5, A6, A7 and A8) in the Changjiang River, no significant (one-way ANOVA test, \(p > 0.05\)) spatial variation of N\(_2\)O concentrations were found in the river during the winter in 2011.

3.2. Excess N\(_2\)O and emission

\(\Delta N_2O\) varied greatly across all the rivers or streams and differences in \(\Delta N_2O\) were significant (ANOVA, \(a = 0.05\), \(P < 0.001\)). The highest \(\Delta N_2O\) were observed in the Nanfei River during 2006–2009 and the lowest \(\Delta N_2O\) were found in the Changjiang River during 2009–2011 (Fig. 2e).

Significant seasonal \(\Delta N_2O\) variations were observed in 5 rivers (Fig. 3). In Changjiang River, West Jilong River and North Jilong River, higher \(\Delta N_2O\) were found from July to October than in cooler months (Fig. 3a, d, f). In contrast, Nanfei River and Hangbu River had higher \(\Delta N_2O\) in colder months (Fig. 3b–c). N\(_2\)O emissions ranged from 0.51 to 2453 μg N m\(^{-2}\) h\(^{-1}\). Changjiang River had the lowest and Nanfei River had the highest N\(_2\)O emissions values of all the rivers analyzed. Differences in N\(_2\)O emissions across all the rivers and streams were statistically significant (ANOVA, \(a = 0.05\), \(P < 0.001\)) (Fig. 2f).

Seasonal variations in N\(_2\)O emissions were found in every river analyzed. In general, there appeared to be two seasonal patterns of N\(_2\)O emissions. While some rivers (e.g., Changjiang River in June and North Jilong River in October) exhibited a single peak (Fig. 3a, f), the majority of the river systems investigated showed double peaks of N\(_2\)O emission (e.g., Nanfei River and Hangbu River in June and November; West Jilong River in February and September; and Zhuxi Stream in April and September) (Fig. 3b–e).

4. Discussions

4.1. The effect of DO and N levels on N\(_2\)O production

Generally, the rivers chosen for study can be divided into two types: runoff rivers which receive significant agricultural runoff (Changjiang River, Hangbu River, West Jilong River, North Jilong River and Zhuxi Stream), and urban rivers which receive significant urban effluents (Nanfei River). The component of DIN varied in different rivers as described above. In Nanfei River, DIN was primarily comprised of NH\(_4\)\(^+\), whereas for runoff rivers, the opposite pattern in DIN composition was observed (high NO\(_3\), low NH\(_4\)\(^+\)). In the urban river, high NH\(_4\)\(^+\) come from the decomposition of organic nitrogen in urban effluents, while NH\(_4\)\(^+\) cannot be oxidized to NO\(_3\) rapidly under hypoxic conditions in urban rivers (Yang et al., 2011; Yu et al., 2013). On the contrary, for runoff rivers, NO\(_3\) is easy leaching with subsurface runoff or groundwater (NH\(_4\)\(^+\) oxidized to NO\(_3\) in groundwater and recharge to river channel), NO\(_3\)\(^-\) dominant DIN concentrations in runoff rivers as a result (Boyer et al., 2006; Garnier et al., 2006).

A general trend across all rivers was found. There was significant positive correlation between DIN and \(\Delta N_2O\) (\(r^2 = 0.20\), \(P < 0.001\)) in all the rivers studied, suggesting that NO\(_3\) production was strongly influenced by N levels in the water column (Fig. 4a). In addition, \(\Delta N_2O\) was significantly positively related to NO\(_3\) concentrations (\(r^2 = 0.20\), \(P < 0.001\)) in runoff rivers (Fig. 4b), indicating that NO\(_3\) levels strongly influence N\(_2\)O production in those rivers. Other

**Table 3**

| Rivers        | N\(_2\)O saturations (mean) | Sampling date       | Timescale | References         |
|--------------|-----------------------------|---------------------|-----------|-------------------|
| 10 streams   | 276–330 % (2905)            | Jun, 2006; Jul, 2007 | Diei      | Bauch et al., 2012 |
| Canada       | 150–8000 % (2165)           | May, 2006–Jun, 2007 | Diei/      | Rosamond et al., 2011 |
| Grand River  | 90–140 % (115%)             | Jul, 2007            | Diei      |                   |
| Eramosa River| Speed River                | 90–800 % (350%)      | Jul, 2006 | Diel              |
| Ohio River   | 160–740 % (230%)            | 2008–2009            | Season    | Beaulieu et al., 2011 |
| Kalamazoo River | 45–135 % (236%)        | 2004–2005            | Season    | Beaulieu et al., 2008 |
| Li River     | 201–404 % (3025)            | Apr–Sep, 2004       | Season    | Clough et al., 2006 |
| Millstone River | 104–123 % (110%)         | Mar, 2001            | Diei      | Laursen and Seitzinger, 2004 |
| Irocious River | 102–209 % (1513)         | May, 2000            | Diel      |                   |
| Hudson River | 185 ± 41.0 % (1513)         | 1998–1999            | Season    | Cole and Caraco, 2001 |
| Canal Two Stream | 100 % (6000%)                | Jul, 2001            | Diel      | Harrison et al., 2005 |
| Changjiang River | 129–140 % (135%)        | Aug, Oct, 2002      | Season    | Yan et al., 2004   |
| Changjiang River | 216 ± 54.2 % (3113)       | Jun–Dec, 2009, 2011 | Season    | This study         |
| Jilong River | 144–967 % (1826%)          | 2006–2009            | Season    | This study         |
| 2 rivers in  | 90–8213 % (1826%)          | 2006–2009            | Season    | This study         |
| Chaobu       | South Plate River          | 80%–2500%           | 1994–1995 | McMahon and Dennehy, 1999 |
| San Joaquin River | 43%–729%              | 2010–2011            | Season    | Hinchaw and Dahlgren, 2013 |
| 5 streams in Canada | 6%–1700%              | 2006–2008            | Season    | Bauch et al., 2012 |
investigators have found similar relationships between NO$_3^-$ and N$_2$O production in agricultural rivers (Herrman et al., 2008; Silvennoinen et al., 2008), although Clough et al. (2006) found no significant relationship between NO$_3^-$ and N$_2$O fluxes in a spring-fed river. However, the relationship between NO$_3^-$ and ΔN$_2$O was not significant ($r^2 = 0.06, p = 0.29$) in Nanfei River. On the contrary, we found a significant positive relationship ($r^2 = 0.21, p = 0.02$) between NH$_4^+$ and ΔN$_2$O (Fig. 4c–d) in Nanfei River, and a similar relationship between NH$_4^+$ and N$_2$O saturation has been found in some other urban rivers (Yu et al., 2013).

DO concentrations were greater than 4.6 mg L$^{-1}$ (7.97 ± 1.19 mg L$^{-1}$) in runoff rivers. A negative correlation between DO and ΔN$_2$O (Fig. 4e, $r^2 = 0.22, P < 0.001$) was found in all the sampling rivers. Meanwhile, a positive correlation between ΔN$_2$O and AOU (Fig. 4f; ΔN$_2$O = 0.55 AOU – 1.37, $R^2 = 0.17, P < 0.001$) was found in runoff rivers. AOU reflects the amount of O$_2$ consumed by remineralization of organic matter and nitrification in a water parcel since its last contact with the surface. The strong correlation between AOU and ΔN$_2$O observed in those rivers provides circumstantial evidence that nitrification is the dominant mechanism of N$_2$O production (Yoshinari, 1976; Cohen and Gordon, 1979). On the other hand, hypoxic conditions were found in the urban Nanfei River (DO = 1.57 ± 1.01 mg L$^{-1}$), and DO showed a positive relationship with ΔN$_2$O ($r^2 = 0.10, p = 0.12$). These results indicate that N$_2$O may be produced by denitrification in Nanfei River. In addition, it seems that N$_2$O production is NH$_4^+$ rather than NO$_3^-$ limited in this river, because a significant positive relationship ($r^2 = 0.21, p < 0.05$) between NH$_4^+$ concentration and ΔN$_2$O was found (Fig. 4d).

4.2. Emission factors for N$_2$O production from rivers in China

We used the IPCC method to calculate N$_2$O emission factors (EF5-r) in all the rivers. In the runoff rivers (Changjiang River, Hangbu River, North Jiulong River, West Jiulong River and Zhuxi Stream), our calculated EF5-r values ranged from 0.05% to 0.87%. Specially, the EF5-r values were greater than 1% (the mean value was 7.45 ± 10.1%) in the urban Nanfei river (which is ammonium-
dominated), much greater than the IPCC recommended value (EF5-r = 0.25%, 2006). Our measurements indicated that the EF5-r methodology underestimated most of the study rivers during the sampling period.

In recent years various studies have suggested modifying the IPCC EF5 values to reduce uncertainties (Nevison, 2000; Reay...
et al., 2005; Ivens et al., 2011; Beaulieu et al., 2011; Rosamand et al., 2012). The current equation for EF5-r may be appropriate for groundwater systems where gas exchange with the atmosphere is limited, but gases exchange rapidly with the atmosphere open stream channels. Therefore, the IPCC emission factor may underestimate N2O production from open channels because it does not account for the dissolved N2O in equilibrium with the atmosphere (Beaulieu et al., 2008). On the other hand, some studies reported that NO3 concentrations did not limit river N2O production (Clough et al., 2006; Rosamand et al., 2012). For example, Rosamand et al. (2012) suggested that N2O production was limited by DO concentration. Therefore, more predictors, such as DO, should be considered in N2O emissions models.

Here, we predicted N2O production using stepwise multiple regressions that include DO, NO3 concentrations and DO levels in the Changjiang river. Stepwise regressions that include DO, NO3 concentrations and DO are better predictors of N2O in urban rivers, explaining 64% of variability in N2O production (Table 4). Similarly, Yu et al. (2013) suggested that water NH4 and DO level had great control on N2O production and were better predictors of N2O emission in some urban rivers in China.

4.3. Uncertainty of gas transfer on N2O emissions

Uncertainty in modeling of gas transfer is significant, especially in our deep rivers. Our results show a mean uncertainty of –10% in k400 value in the Changjiang River. As a result, the effect of this uncertainty on N2O emissions from the Changjiang River is averaged to 11%, sometimes is up to 27%. On the other hand, we found no significant differences in N2O emissions calculated by two gas transfer models in Nanfei River (ANOVA, p = 0.792), Hanghu River (ANOVA, p = 0.608), Zhuxi Stream (ANOVA, p = 0.888), North Jiulong River (ANOVA, p = 0.507) and West Jiulong River (ANOVA, p = 0.461). However, the overall accuracy of this model-based estimation remains uncertain because it depends on the accuracy of the underlying model structure which can be tested only by using measurements of gas transfer velocity (Baulch et al., 2011). Direct measurement on gas transfer is beyond this study but deserve further study to improve accuracy of estimating N2O emission from China rivers.

5. Conclusions

Spatial and temporal variations of riverine N2O concentration and production from three watershed in China with varying size and characteristics were investigated. N2O concentrations were significantly higher in an urban river than in runoff rivers. Different seasonal and diurnal patterns of ∆N2O were found with complex controlling factors in different rivers. There appeared to be two seasonal patterns of N2O emissions. While some rivers exhibited a single peak, the majority of the river systems investigated showed double peaks of N2O emission. There were no significant differences in diurnal patterns (day vs. night) of N2O concentrations and saturations in the Changjiang river. Stepwise regression models of N2O production from various kinds of rivers were built based on the dynamics of DO and N levels. The results showed that NO3 and DO are better predictors of N2O in runoff rivers, while NH4 and DO level had great control on N2O production in urban rivers.

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| Rivers         | Model                             | Step | R square | Standardized coefficients | Sig.  |
|---------------|----------------------------------|------|----------|---------------------------|-------|
| Runoff river  | ∆N2O = −0.12 [DO] + 0.15 [NO3] + 7.2 | 1    | 0.44     | <0.001                    | DO    |
| Urban river   | ∆N2O = −1.35 [NH4] + 3.32 [DO] + 15.6 | 1    | 0.43     | 0.008                     | NH4   |
| All rivers    | ∆N2O = −0.14 [DIN] − 0.05 [DO] + 0.52 | 1    | 0.30     | 0.002                     | DO    |

* Rivers that receiving significant agricultural runoff inputs (such as the Changjiang River, the Hanghu River, the West Jiulong River, the North Jiulong River and the Zhuxi Stream).
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