Effect of dissolved oxygen and nitrogen on emission of N₂O from rivers in China

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HIGHLIGHTS

- Demonstrate heterogeneous pattern of N₂O concentration and emission in various rivers.
- N₂O in urban river were significantly higher than those in agricultural runoff rivers.
- NO₃⁻ and DO explaining 47% variability in N₂O production in runoff rivers.
- NH₄⁺ and DO explaining 64% variability in N₂O production in urban rivers.

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ABSTRACT

Six rivers from three watersheds in China were chosen to study the temporal and spatial variations in nitrous oxide (N₂O) concentrations and emissions in order to examine the link between N₂O 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 N₂O concentrations were 0.15–1.07 (mean 0.51) and 0.22–22.7 (mean 4.10) $\mu\text{g N L}^{-1}$ in runoff rivers and an urban river, respectively. N₂O was oversaturated in almost all the rivers, suggesting that the rivers were sources of atmospheric N₂O. N₂O emissions in the urban river (range from 1.53 to 2453, mean 529 $\mu\text{g N m}^{-2} \text{h}^{-1}$) were significantly higher than those in runoff rivers (range from 0.51 to 80.9, mean 18.0 $\mu\text{g N m}^{-2} \text{h}^{-1}$). We found a significant positive correlation of N₂O production with NO₃⁻ ($r^2 = 0.30$, $p < 0.001$) and a negative correlation of N₂O production with DO concentrations ($r^2 = 0.22$, $p < 0.001$) in runoff rivers. Particularly, there existed a significant positive relationship ($r^2 = 0.21$, $p < 0.001$) between NH₄⁺ and N₂O production in an urban river. By using stepwise regression analysis, we found N₂O production can be predicted by the dynamics of DO and N levels: for runoff rivers, NO₃⁻ and DO explained 47% variability in N₂O production, while for the urban river, NH₄⁺ and DO explained 64% variability in N₂O production. We suggest that the IPCC method to calculate N₂O emission factors should be revised in view of the importance of these multiple factors.

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1. Introduction

Nitrous oxide (N₂O) 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 N₂O emissions from terrestrial and aquatic ecosystems, and increased atmospheric N₂O (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 N₂O production and emission from diverse rivers respond significantly to increasing anthropogenic N loading (Cole and Caraco, 2001;

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Garnier et al., 2006). Numerous investigations have reported strong correlations between dissolved N_2O and NO_3^- concentration in river waters (Herrman et al., 2008; Silvennoinen et al., 2008). Yan et al. (2012) concluded that NO_3^- is a valid predictor of river N_2O 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 N_2O occurred without any concurrent transformation of the NO_3^- in a spring fed river where no significant relationship between NO_3^- and N_2O was found. Rosamond et al. (2012) reported that N_2O 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 N_2O emission. In contrast to NO_3^- , several investigators have demonstrated a negative correlation between DO and dissolved N_2O (Yoshinari, 1976; Zhan and Chen, 2006; Rosamond et al., 2011, 2012).

To facilitate estimation of N_2O 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 N_2O in river networks. This value was three times greater than that estimated using IPCC methodology. On the other hand, some studies reported that NO_3^- concentrations did not limit river N_2O production (Clough et al., 2006; Rosamond et al., 2012). Therefore, quantifying riverine N_2O 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 N_2O production in river systems (Seitzinger, 1988; Bouwman, 1996), and riverine N_2O emission from China has a measurable impact on

Fig. 1. The location of the three watersheds and sampling stations.

global N₂O emission from aquatic systems (Seitzinger and Kroeze, 1998). Thus far, most reports have focused on N₂O 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 N₂O 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 N₂O 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 N₂O concentrations from diverse rivers; 2) investigate the links between N₂O production, DO and inorganic N levels in river systems, and 3) build N₂O predictive models for various kinds of rivers based on the relationship between N₂O 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 (6.4×10^3 km) in the world, with an average annual discharge of 10×10^{11} m³. The basin (24°27'–35°54'N, 90°13'–122°19'E) covers an area of 1.8×10^6 km². The average annual temperature is 16–18 °C, and the average rainfall is 1.1×10^3 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 1.3×10^4 km², 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 1.5×10^8 m³/yr, while the Hangbu River receives significant inputs from agricultural runoff (>80%), and has an average discharge of 19.3×10^8 m³/yr. The Jiulong River watershed (116°47'–118°02'E, 24°24'–25°53'N), with a catchment area of 1.47×10^4 km², is

located in southeastern China. The Jiulong River discharges about 12.4×10^9 m³/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 1.6×10^3 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 N₂O 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 NO₃⁻ and NH₄⁺ 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
Physical and chemical characteristics of the study rivers at the 13 sampling sites.

Study rivers ^a	Catchment area (km ²)	Sampling sites ^b	Location		River length (km)	River width (m)	River depth (m)	DIN (mg/L)		Dominant land use (%) ^c
			E	N				NO ₃ -N	NH ₄ -N	
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	
		A3	117°02'	30°31'	5650	1310	14	0.86	0.30	
		A4	114°04'	30°38'	5264	980	24	1.94	0.17	
	1,333,200	A5	108°25'	30°45'	4226	750	90	1.56	0.06	Forest (>60)
		A6	106°36'	29°37'	3905	760	20	1.49	0.05	
		A7	111°29'	28°54'	1570	270	5.3	3.09	0.14	
		A8	106°25'	29°51'	1119	172	26	1.75	0.11	
NFR	1618	B1	117°22'	31°49'	65	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)

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

^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); Zhengdian station (C2); Zhuxi station (C3).

^c Data from Yan et al., 2010, 2012; Yang et al., 2011.

2.3. Analytical methods

Dissolved N₂O 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 N₂ (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).

N₂O 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 N₂O concentrations (C_w) in water samples were determined using the method described in Johnson et al. (1990). Filtered water samples were analyzed for NH₄⁺ 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 N₂O saturation was calculated by the following equation,

$$N_2O \text{ saturation} = [N_2O_{meas}] / [N_2O_{equ}] \times 100\% \quad (1)$$

Where, $[N_2O_{meas}]$ is the measured N₂O concentration ($\mu\text{g N L}^{-1}$), and $[N_2O_{equ}]$ is the equilibrium N₂O concentration of river water with the atmosphere ($\mu\text{g N L}^{-1}$), which was calculated using Henry's Law (Lide and Fredrikse, 1995).

The excess N₂O (ΔN_2O , $\mu\text{g N L}^{-1}$) is defined as the difference between $[N_2O_{meas}]$ and $[N_2O_{equ}]$.

$$\Delta N_2O = [N_2O_{meas}] - [N_2O_{equ}] \quad (2)$$

Water surface emissions of N₂O were recalculated based on the gas transfer velocity and ΔN_2O (Raymond and Cole, 2001; Garnier et al., 2006):

$$F = \Delta N_2O \times k_{N_2O} \quad (3)$$

Where, F is the water surface emissions of N₂O ($\mu\text{g N m}^{-2} \text{ h}^{-1}$), and k_{N_2O} (cm h^{-1}) is the gas transfer velocity.

k_{N_2O} was calculated by the following equation (Wanninkhof, 1992):

$$k_{N_2O} = k_{600} \times (Sc_{N_2O}/600)^{-n} \quad (4)$$

Where, Sc_{N_2O} is the Schmidt number for N₂O 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).

$$k_{600} = 3.3(\pm 1.6) + 4.2(\pm 0.6) \times u_{10} \quad (5)$$

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:

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

Where w 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, $\alpha = 0.05$, $p = 0.232$) of k_{600} values by equations (5) and (6) for those rivers with a water flow rate lower than 0.5 m s^{-1} (Nanfei 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 N₂O emissions is discussed in section 4.3.

We calculated the river N₂O emission factor ($EF5-r$; IPCC, 2006) to compare to IPCC predictions based on NO₃, $EF5-r$ is calculated as:

$$EF5-r = [N_2O - N] / [NO_3^- - N] \times 100\% \quad (7)$$

where, $EF5-r$ is the river N₂O emission factor (%), $[N_2O - N]$ is the dissolved N₂O concentration ($\mu\text{g N L}^{-1}$), and $[NO_3^- - N]$ is the water NO₃ concentration ($\mu\text{g N L}^{-1}$).

Apparent oxygen utilization (AOU, mg L^{-1}) is defined as the difference between the measured oxygen content and the

Table 2
Gas transfer velocity (K_{600}) of the 6 study rivers at 13 sampling sites.

Study rivers	Sampling sites	Wind speed	Flow rate	River temperature	K_{600} (cm h^{-1}) ^a	
		m s^{-1}	m s^{-1}		Eq. 5	Eq. 6
CR	A1	0.8–2.8	0.56 –1.34	9.8–30.0	3.50 –11.7	2.73 –8.68
	A2	1.1–2.5	0.55 –1.27	11.0–29.0	5.66 –10.7	4.23 –7.39
	A3	1.0–2.4	0.51 –1.10	13.3–27.1	5.30 –10.3	4.01 –7.64
	A4	0.7–0.8	1.60 –1.80	17.5–17.8	7.80 –7.95	3.10 –3.95
	A5	0.6–0.7	0.41 –0.53	18.3–18.7	3.31 –3.52	2.91 –3.10
	A6	1.0–1.3	0.31 –0.51	20.1–20.5	7.90 –8.00	3.74 –3.81
HR	A7	0.9–1.1	1.00 –1.12	16.0–16.3	5.31 –5.39	4.55 –4.60
JLR	A8	0.7–0.9	0.17 –0.20	19.1–19.7	3.20 –3.78	3.10 –3.52
NFR	B1	1.4–5.0	0.05 –0.21	7.0–30.5	10.6 –21.5	10.3 –19.4
HBR	B2	1.5–5.0	0.07 –0.30	6.5–27.0	11.4 –25.3	11.9 –20.3
ZXS	C1	0.1–2.4	0.14 –0.82	14.8–30.2	2.02 –10.3	2.56 –8.52
NJR	C2	0.1–2.2	0.08 –0.35	15.0–31.0	1.98 –13.2	1.47 –9.49
WJR	C3	0.1–1.9	0.05 –0.43	15.2–31.2	2.00 –8.58	1.76 –6.46

^a Eq. (5) (Alin et al., 2011) accounting for wind speed and used in rivers with low water flow rate, while Eq. (6) (Borges et al., 2004) accounting for both wind speed and water flow rate and used in deep rivers with water flow rate higher than 0.5 m s^{-1} .

saturation oxygen content of river water (Yoshinari, 1976; Cohen and Gordon, 1979), as shown in equation (8).

$$AOU = [DO_{sat}] - [DO_{meas}] \quad (8)$$

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 ΔN_2O , DO, NO_3^- , DIN, AOU and water temperature. Spatial differences in N_2O , DO, ΔN_2O and N_2O

emissions were analyzed using one-way ANOVA ($\alpha = 0.05$). Regression analysis between N_2O 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_2O concentrations

DO concentrations varied widely across the sampled sites,

Fig. 2. Distribution of river chemistry, nitrous oxide (N_2O) concentrations, N_2O production and emission (A. dissolved oxygen (DO) concentration; B. nitrate (NO_3^-) concentration; C. ammonia (NH_4^+) concentration (in log-scale); D. N_2O concentration (in log-scale); E. N_2O production (in log-scale); F. N_2O emission (in log-scale)).

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, NO₃⁻, NH₄⁺ and DIN (NO₃⁻ + NH₄⁺) 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 NH₄⁺–N fraction, which represented more than 90% of DIN on average. In all other rivers, DIN was dominated by the NO₃⁻–N fraction, which represented 60% of the DIN fraction on average.

N₂O concentrations ranged from 0.15 to 22.7 µg N L⁻¹ at all sites. The highest N₂O concentrations were observed in the Nanfei River and the lowest N₂O concentrations were found in the Hangbu River during 2006–2009 (Fig. 2d). Most of rivers/streams were super saturated with N₂O (90–8213% saturation) during the sampling period. Compared to reports for other rivers around the world (Table 3), the N₂O super-saturations were typically low in the Changjiang River, but extremely high (more than 1000%) in the Nanfei River. Over the two 60-h periods in August and October, concentrations of N₂O ranged from 0.26 to 0.34 µg N L⁻¹ (saturation ranged from 154% to 198%) and from 0.44 to 0.52 µg N L⁻¹ (saturation ranged from 209% to 235%), respectively. During day-time (10:00–16:00), N₂O concentrations varied from 0.26 to 0.31 µg N L⁻¹ in August and from 0.44 to 0.50 µg N L⁻¹ in October. At

night (22:00–4:00), N₂O concentrations varied from 0.28 to 0.34 µg N L⁻¹ in August and from 0.45 to 0.52 µg 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 N₂O concentrations and saturations over a consecutive 60-h period in each observation in the Changjiang River. On the other hand, N₂O concentrations ranged from 0.64 to 0.81 µg N L⁻¹ with an average of 0.72 ± 0.05 µg 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 N₂O concentrations were found in the river during the winter in 2011.

3.2. Excess N₂O and emission

ΔN₂O varied greatly across all the rivers or streams and differences in ΔN₂O were significant (ANOVA, $\alpha = 0.05$, $P < 0.001$). The highest ΔN₂O were observed in the Nanfei River during 2006–2009 and the lowest ΔN₂O were found in the Changjiang River during 2009–2011 (Fig. 2e).

Significant seasonal ΔN₂O variations were observed in 5 rivers (Fig. 3). In Changjiang River, West Jiulong River and North Jiulong River, higher ΔN₂O were found from July to October than in cooler months (Fig. 3a, d, f). In contrast, Nanfei River and Hangbu River had higher ΔN₂O in colder months (Fig. 3b–c).

N₂O emissions ranged from 0.51 to 2453 µg N m⁻² h⁻¹. Changjiang River had the lowest and Nanfei River had the highest N₂O emissions values of all the rivers analyzed. Differences in N₂O emissions across all the rivers and streams were statistically significant (ANOVA, $\alpha = 0.05$, $P < 0.001$) (Fig. 2f).

Seasonal variations in N₂O emissions were found in every river analyzed. In general, there appeared to be two seasonal patterns of N₂O emissions. While some rivers (e.g., Changjiang River in June and North Jiulong River in October) exhibited a single peak (Fig. 3a, f), the majority of the river systems investigated showed double peaks of N₂O emission (e.g., Nanfei River and Hangbu River in June and November; West Jiulong 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 N₂O 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 Jiulong River, North Jiulong 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 NH₄⁺, whereas for runoff rivers, the opposite pattern in DIN composition was observed (high NO₃⁻, low NH₄⁺). In the urban river, high NH₄⁺ come from the decomposition of organic nitrogen in urban effluents, while NH₄⁺ cannot be oxidized to NO₃⁻ rapidly under hypoxic conditions in urban rivers (Yang et al., 2011; Yu et al., 2013). On the contrary, For runoff rivers, NO₃⁻ is easy leaching with subsurface runoff or groundwater (NH₄⁺ oxidized to NO₃⁻ in groundwater and recharge to river channel), NO₃⁻ 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 ΔN₂O ($r^2 = 0.20$, $P < 0.001$) in all the rivers studied, suggesting that N₂O production was strongly influenced by N levels in the water column (Fig. 4a). In addition, ΔN₂O was significantly positively related to NO₃⁻ concentrations ($r^2 = 0.30$, $P < 0.001$) in runoff rivers (Fig. 4b), indicating that NO₃⁻ levels strongly influence N₂O production in those rivers. Other

Table 3
Summary of nitrous oxide (N₂O) saturations in various rivers in the literature and this study.

Rivers	N ₂ O saturations (mean)	Sampling date	Timescale	References
10 streams in Canada	276–303 % (290%)	Jun, 2006; Jul, 2007	Diel	Baulch et al., 2012
Grand River	150–8000 % (216%)	May, 2006–Jun, 2007	Diel/Season	Rosamond et al., 2011
Eramosa River	90–140 % (115%)	Jul, 2007	Diel	
Speed River	90–800 % (350%)	Jul, 2006, 2007	Diel	
Ohio River	160–740 % (230%)	2008–2009	Season	Beaulieu et al., 2011
Kalamazoo River	45–1358 % (236%)	2004–2005	Season	Beaulieu et al., 2008
Lli River	201–404 % (302%)	Apr–Sep, 2004	Season	Clough et al., 2006
Millstone River	104–123 % (110%)	Mar, 2001	Diel	Laursen and Seitzinger, 2004
Iroquois River	102–209 % (151%)	May, 2000	Diel	
Hudson River	185 ± 43.0%	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%	Jun –Dec, 2009, 2011	Diel/Season	This study
Jiulong River	144–967 % (311%)	Jen–Dec, 2010.	Season	This study
2 rivers in Chaohu	90–8213 % (1826%)	2006–2009	Season	This study
South Platte River	80%–2500%	1994–1995	Season	McMahon and Dennehy, 1999
San Joaquin River	43%–729%	2010–2011	Season	Hinshaw and Dahlgren, 2013
5 streams in Canada	6%–1700%	2006–2008	Season	Baulch et al., 2012

Fig. 3. Seasonal variations of nitrous oxide apparent production ($\Delta\text{N}_2\text{O}$), nitrate (NO_3^-) and ammonia (NH_4^+).

investigators have found similar relationships between NO_3^- and N_2O 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 $\Delta\text{N}_2\text{O}$ fluxes in a spring-fed river. However, the relationship between NO_3^- and $\Delta\text{N}_2\text{O}$ 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 $\Delta\text{N}_2\text{O}$ (Fig. 4c–d) in Nanfei River, and a similar relationship between NH_4^+ and N_2O saturation has been found in some other urban rivers (Yu et al., 2013).

DO concentrations were greater than 4.6 mg L^{-1} ($7.97 \pm 1.19 \text{ mg L}^{-1}$) in runoff rivers. A negative correlation between DO and $\Delta\text{N}_2\text{O}$ (Fig. 4e, $r^2 = 0.22$, $P < 0.001$) was found in all the sampling rivers. Meanwhile, a positive correlation between $\Delta\text{N}_2\text{O}$ and AOU (Fig. 4f, $\Delta\text{N}_2\text{O} = 0.55 \text{ AOU} - 1.37$, $R^2 = 0.17$, $P < 0.001$) 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 $\Delta\text{N}_2\text{O}$ observed in those rivers provides

circumstantial evidence that nitrification is the dominant mechanism of N_2O production (Yoshinari, 1976; Cohen and Gordon, 1979). On the other hand, hypoxic conditions were found in the urban Nanfei River ($\text{DO} = 1.57 \pm 1.01 \text{ mg L}^{-1}$), and DO showed a positive relationship with $\Delta\text{N}_2\text{O}$ ($r^2 = 0.10$, $p = 0.12$). These results indicate that N_2O may be produced by denitrification in Nanfei River. In addition, it seems that N_2O 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 $\Delta\text{N}_2\text{O}$ was found (Fig. 4d).

4.2. Emission factors for N_2O production from rivers in China

We used the IPCC method to calculate N_2O 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 $7.45 \pm 10.1\%$) in the urban Nanfei river (which is ammonium-

Fig. 4. Relationship between nitrous oxide apparent production (ΔN_2O) and river chemistry parameters (A. ΔN_2O (in log-scale) and dissolved inorganic nitrogen (DIN) for all rivers; B. ΔN_2O and nitrate (NO_3^-) for runoff rivers; C. ΔN_2O and ammonium (NH_4^+) for runoff rivers; D. ΔN_2O and NH_4^+ for urban rivers; E. ΔN_2O (in log-scale) and dissolved oxygen (DO) concentration for all rivers; F. ΔN_2O and river apparent oxygen utilization (AOU) for runoff rivers.).

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

Table 4N₂O production models for various kinds of rivers by using stepwise multiple regressions.

Rivers	Model	Step	R square	P	Standardized coefficients	Sig.
Runoff river ^a	$\Delta\text{N}_2\text{O} = -0.12 [\text{DO}] + 0.15 [\text{NO}_3^-] + 7.2$	1	0.44	<0.001	DO	-0.349
		2	0.47	<0.001	NO ₃ ⁻	0.168
Urban river ^b	$\Delta\text{N}_2\text{O} = 1.35 [\text{NH}_4^+] + 3.32 [\text{DO}] + 15.6$	1	0.43	0.008	NH ₄ ⁺	0.799
		2	0.64	0.002	DO	0.485
All rivers	$\Delta\text{N}_2\text{O} = 0.14 [\text{DIN}] - 0.05 [\text{DO}] + 0.52$	1	0.30	0.002	DIN	0.606
		2	0.46	0.001	DO	-0.404

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

^b Rivers that dominate by urban effluents (e.g. the Nanfei River).

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 in 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⁻, NH₄⁺, water temperature, pH and wind speed. The results showed that NO₃⁻ and DO are better predictors of N₂O in runoff rivers, explaining 47% of variability in N₂O production (Table 4). On the other hand, NH₄⁺ and DO are superior 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 *k*₆₀₀ 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 difference of N₂O emissions calculated by two gas transfer models in Nanfei River (ANOVA, *p* = 0.792), Hangbu 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 watersheds 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 ΔN₂O 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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