

SEASONAL PATTERN OF N₂O CONCENTRATIONS AND EMISSIONS IN THE SEWAGE-ENRICHED RIVERS: CASE OF CHAOHU LAKE BASIN IN SOUTHEAST CHINA

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(Received 23rd Nov 2018; accepted 1st May 2019)

Abstract. Two sewage-enriched urban rivers within Chaohu Lake Basin in Southeast China were selected to study the seasonal variations in Nitrous Oxide (N₂O) concentrations, to improve the information of N₂O concentrations and emissions in the similar areas. The results indicate that N₂O concentrations ranged 16.12~1043.09 nmol/L and averaged 266.27 ± 250.28 nmol/L during the sampling period. N₂O was oversaturated in both rivers ranging 184~12084% (mean 2964%). The significantly higher level of N₂O concentrations and emissions were observed in cold months. It is indicated that the two rivers were net sources of atmospheric N₂O. N₂O emissions ranged 11.32~2920.38 µg N-N₂O/m²/h with an overall mean value of 743.57 ± 831.78 µg N-N₂O/m²/h. A significant negative correlation exists between N₂O concentration and water temperature, which may be regulated by inverse tendencies between temperature and riverine nutrient loadings. Dissolved Oxygen (DO) is a predictor of N₂O in Nanfei River explaining 60% of variability in N₂O; while water temperature and NO₃⁻ are better predictors of N₂O in Ershibu River explaining 73% of variability in N₂O. The riverine N₂O may be produced by denitrification in Nanfei River while by coupled nitrification-denitrification in Ershibu River.

Keywords: *nitrous oxide, concentration, nitrification, flux, urban river*

Introduction

Nitrous Oxide (N₂O) is one of the most significant greenhouse gases contributing to the destruction of stratospheric ozone and climate change (Ravishankara et al., 2009; Wójcik-Gront et al., 2015; Pauleta, et al., 2019). The atmospheric N₂O has risen from about 270 ppb in the pre-industrial era to 319 ppb in the present, mainly due to human perturbations of the global nitrogen (N) cycle (Holland et al., 2005). As N inputs increase, potentially more N₂O is produced (Bouwman, 1995; Wójcik-Gront et al., 2015). In river networks, more than 0.68 Tg/yr of anthropogenic N inputs were converted to N₂O on the global scale, equivalent to 10% of the anthropogenic N₂O emission rate (Beaulieu et al., 2011; Quick et al., 2019; Luo et al., 2019). Therefore, more and more attentions have been paid to the emissions of N₂O from different sources as accurate information is required to determine the contribution of N₂O to global greenhouse gas fluxes (Khalil et al., 2002; Yang and Lei, 2018).

Among the many natural and anthropogenic N₂O sources, most are biological ones (Short et al., 2013). In aquaculture systems, N₂O can be produced by denitrification under anaerobic conditions, where NO₃⁻ was converted to N₂O and dinitrogen (N₂)

(Öquist et al., 2004). Under oxic conditions, N₂O is also produced as a by-product of nitrification where ammonium (NH₄⁺) was oxidized to nitrite (NO₂⁻), and subsequently to NO₃⁻ (Stein and Yung, 2003). Natural rivers have shown large temporal and spatial variations in their N₂O production and emissions due to the changes of topographic feature and environmental factors (Wilcock et al., 1998; Bansal et al., 2015; Quick et al., 2019). The exact mechanisms of aquatic N₂O production are related to the various specific environmental conditions, such as N species and loads, dissolved oxygen (DO) concentration, pH, and others. The classification of carbon source also influences N₂O emission from denitrification and nitrification. Controlling factors related to N₂O production and emissions in rivers are still needed to fully understand due to lack of *in situ* observation data. Thus, more investigation is needed to determine the underlying mechanism of seasonal variation in N₂O concentration in rivers.

Emissions of N₂O from riverine ecosystems take significant influences on the global climate change, since riverine ecosystems are very sensitive to human activities and often receive high loadings of nutrient and organic matter (Richey et al., 2002; Bansal et al., 2015; Yang and Lei, 2018; Quick et al., 2019). Much work has been dedicated to quantifying N₂O emissions from terrestrial ecosystems; however, emissions of N₂O from rivers and streams have received much less attention and remain a major source of uncertainty in the global N₂O budget. Similar to many developing countries, river N pollution is one of the most critical environmental problems in China (Richey et al., 2002; Yang et al., 2006, 2013; Wang et al., 2007; Luo et al., 2019). The related researches on China's greenhouse gas emission primarily focus on the estuary and coastal areas (Yang et al., 2006; Wang et al., 2007; Liu et al., 2015; Yang and Lei, 2018). However, few studies actually directly measure N₂O fluxes from N enriched rivers, and that information is sparse.

Chaohu Lake is a shallow lake in Southeast China, which has suffered from serious pollution resulting from substantial discharge of urban wastewater and agricultural runoff. It has been reported that, the annual mean concentration of Total Nitrogen (TN) and Total Phosphorus (TP) over 2001-2016 ranged 0.08-24.60 and 0.02-2.46 mg/L, respectively, meanwhile, the lake water quality showed no substantial improvement (Yang et al., 2013; Yang and Lei, 2018). The Nanfei River (NR) and Ershibu River (ER) are two urban tributaries of Chaohu Lake. These two rivers are narrow and short with low flow speed. Large amounts of N-enriched sewage inputs into the two rivers result in highly eutrophic river water. Significantly, small rivers are thought to be hot spots of nitrogen cycling (Alexander et al., 2000; Bansal et al., 2015; Quick et al., 2019) and can remove a large proportion of nutrient inputs (Wollheim et al., 2006; Luo et al., 2019; Quick et al., 2019), hence could be important sites of N₂O emissions. Therefore, this study aimed to determine: (1) the presence and extent of seasonal variations in river water chemistry, dissolved N₂O concentration and emissions in sewage-enriched rivers in the Chaohu Lake region; (2) the potential factors that regulate the seasonal N₂O variability.

Materials and methods

Sites description

The study was carried out in NR and ER, two tributaries of Chaohu Lake. The mean annual temperature and precipitation of this region is 15.5 °C and 950 mm respectively. The NR and ER are small rivers with a total length of 70 and 17 km respectively

(Table 1). In this study, the sampling site was set up at the downstream of each river and located at urban areas (Fig. 1). The respective mean water depth of the sampling site is 1.8 m and 3.2 m in NR and ER, and the respective mean flow speed is 0.2 and 0.3 m/s. In recent years, the sewage loading of NR and ER have significantly increased as a result of the effects of local development, which may have become atmospheric N₂O sources. Increases in riverine N and organic matter discharge also stimulate microbial processes and associated algae blooming in Chaohu Lake.

Table 1. Physical characteristics of the study rivers

River	River length (km)	Mean flow speed (m/s)	Mean water depth (m)	Dominant land use (%)	Sampling location
NR	70	0.2	1.8	Urban (> 70)	Daxing port
ER	17	0.3	3.2	Urban (> 80)	Longtang bridge

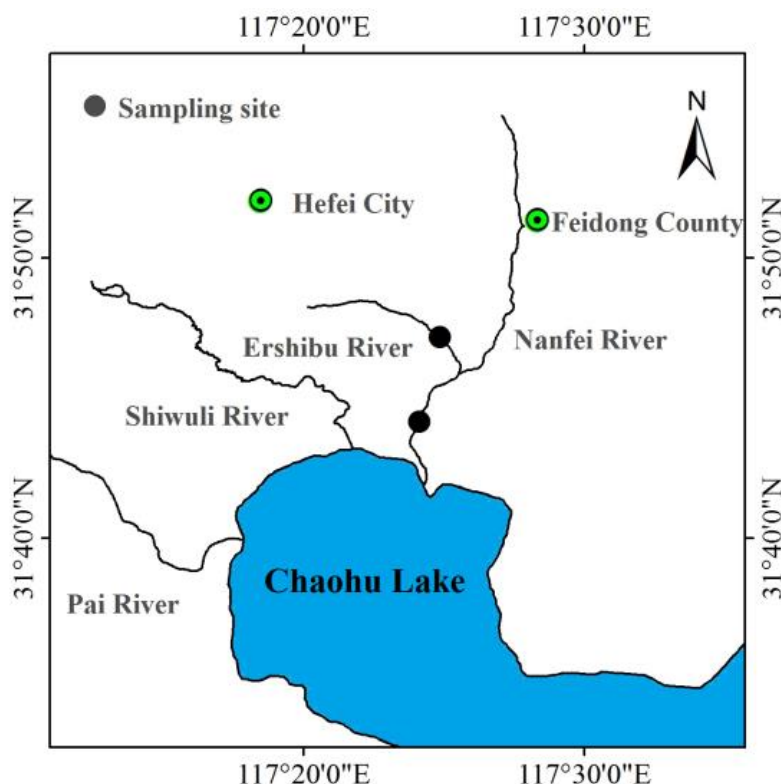


Figure 1. The location of the sampling rivers and sampling sites

Sample collection and chemical analysis

Triplicate surface water (0.2 m depth) samples were collected monthly during Jan. and Dec. in 2017 for the measurement of NH₄⁺, NO₃⁻, TP, BOD₅, COD_{Mn}, SO₄²⁻, and Cl⁻. Dissolved oxygen (DO), pH, and water temperature were measured *in situ* using a portable meter (HQ30D, USA). Samples for dissolved N₂O analysis were collected in 60-ml serum bottles sealed with a butyl-rubber stopper, and preserved after the addition of a few drops of saturated mercuric chloride solution to prevent their biological activities. Water samples were stored in ice box during transport and analyzed within 24 h.

The respective concentration of NH₄⁺, NO₃⁻, TP, BOD₅, COD_{Mn}, SO₄²⁻, and Cl⁻ in water samples was determined according to the standard methodology of GB3838-2002 promulgated by the China central government. The headspace-equilibrium method was used for measurement of initial sample dissolved N₂O concentrations in river water (Huttunen et al., 2002; Liu et al., 2015; Quick et al., 2019; Luo et al., 2019). Twenty milliliters of highly purified N₂ (purity > 99.999%) was injected into the serum bottle using an airtight syringe and a 20-ml water sample was displaced. Bottle headspace N₂O concentrations were directly analyzed using a gas chromatograph (HP5890 II) equipped with an electron capture detector (ECD) after the bottles were vigorously shaken for 4 h. Initial N₂O concentrations (C_w) in water samples were calculated (Johnson et al., 1990; Yang and Lei, 2018). The equilibrium concentration (C_e) of N₂O in river water with atmosphere was calculated using Henry's first law. Dissolved N₂O saturation, expressed in %, was calculated by comparing C_w and C_e.

N₂O emission flux

N₂O emission flux across the water-air interface was estimated using the two-layer model:

$$F = k \times (C_w - C_e) \quad (\text{Eq.1})$$

where F is the N₂O emission flux (μg N-N₂O/m²/h); C_w and C_e is the measured and equilibrium concentration of N₂O (nmol/L), respectively; k (cm/h) is the gas transfer coefficient, calculated by the equation accounting for both wind speed and flow speed (Borges et al., 2004; Liu et al., 2015):

$$k = [1 + 1.719(w/h)^{0.5} + 2.58\mu_{10}](S_c/600)^{-1/2} \quad (\text{Eq.2})$$

where w and h are flow speed (m s⁻¹) and depth (m) of river water column, respectively; μ_{10} (m/s) is the instantaneous wind speed at the 10 m height; S_c is the Schmidt number for N₂O calculated by the equation proposed firstly by Wanninkhof (1992): $S_c = 2301.1 - 151.1t + 4.7364t^2 - 0.059431t^3$, where t (°C) is in situ river water temperature. In this study, wind speed data was gained from the Hefei Meteorologic Bureau, Anhui Province.

Results

Water chemistry

NH₄⁺ and NO₃⁻ concentrations varied considerably over the sampling time, ranging 1.97~23.75 (mean 12.24 ± 5.13) and 0.05~6.98 (mean 3.54 ± 4.45) mg/L (Fig. 2a, b), respectively. NH₄⁺ and NO₃⁻ concentrations indicated a generally higher level in cold months ($P < 0.001$). Difference in mean NH₄⁺ and NO₃⁻ concentrations was not significant between the two rivers ($P > 0.05$). DO concentration ranged 0.20~7.70 mg/L with an overall mean of 2.61 ± 2.14 mg/L (Fig. 2c). In NR, DO concentrations were generally lower than 2 mg/L. Similar to the patterns of NH₄⁺, TP concentrations (ranging 0.20~2.37 mg/L, mean 1.16 ± 0.53 mg/L) showed the marked temporal variations and reached the lowest value in July in both rivers (Fig. 2d). Water temperature ranged 11.0~33.3°C (Fig. 2e), significantly negatively related with DO ($P < 0.05$). The pH value of river water ranged 6.60~8.56 and decreased dramatically after August (Fig. 2f).

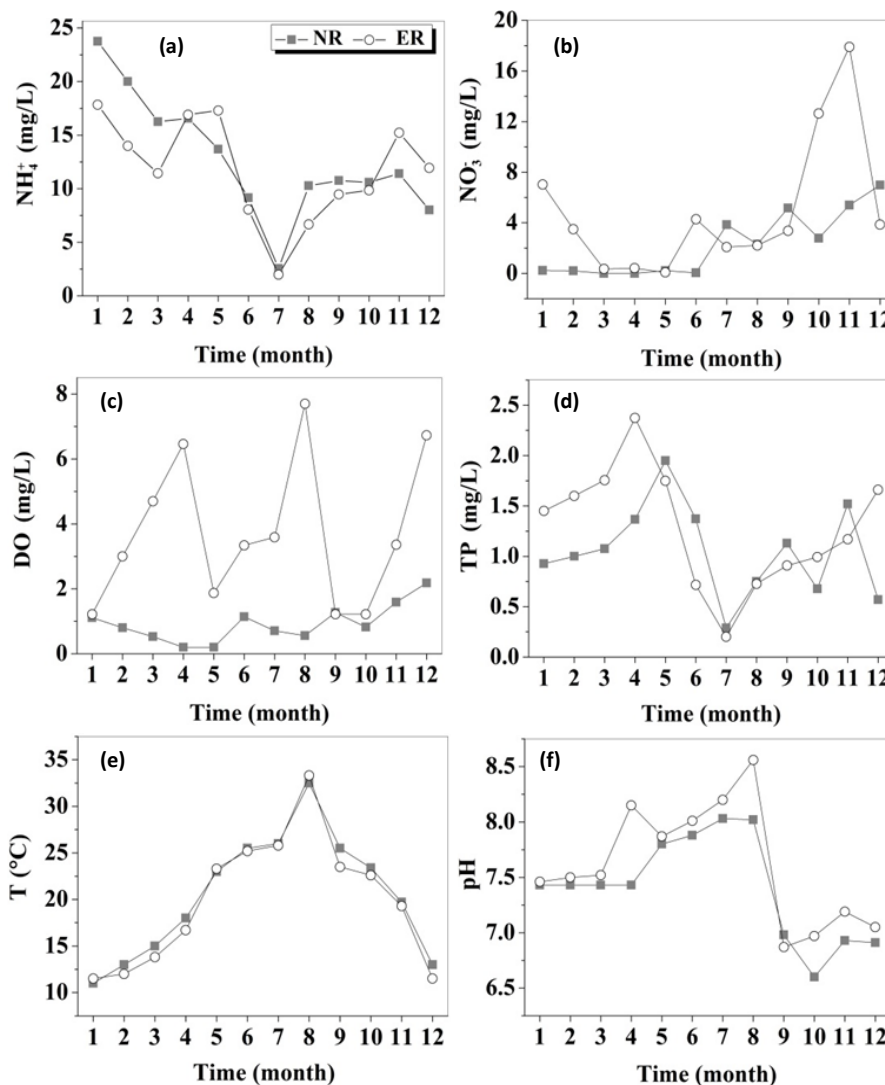


Figure 2. Seasonal variations in NH_4^+ , NO_3^- , DO, TP, water temperature (T), and pH value of Nanfei and Ershibu River

Monthly concentrations of BOD_5 , COD_{Mn} , SO_4^{2-} , and Cl^- in water samples are shown in Table 2. BOD_5 and COD_{Mn} concentrations ranged 3.6–23.1 and 7.5–20.4 mg/L, with an overall mean of 9.80 ± 5.37 and 11.97 ± 4.44 mg/L, respectively. Significantly higher BOD_5 and COD_{Mn} concentrations were investigated in spring and winter ($P < 0.001$). SO_4^{2-} and Cl^- concentrations ranged 45.65–332.50 (mean 101.43 ± 79.06) and 28.55–277.14 (mean 107.16 ± 56.57) mg/L, respectively, generally lower in summer.

Compared to other rivers in this region, the NR and ER showed extremely high level of NH_4^+ , NO_3^- , TP, BOD_5 , COD_{Mn} , SO_4^{2-} , and Cl^- concentrations. The long-term dynamics of water quality in Chaohu river nets were observed over 13 years (Yang et al., 2013; Yang and Lei, 2018), indicating that NH_4^+ , COD_{Mn} , and TP concentrations in the Fengle and Hangbu river which drained agricultural runoff averaged 0.25, 0.07, 4.17 mg/L and 0.31, 0.10, 3.47 mg/L, respectively. Based on the latest investigation, the respective mean SO_4^{2-} and Cl^- concentration was 29.8 and 23.5 mg L⁻¹ in Fengle River, and 57.1 and 37.9 mg/L in Hangbu River.

Table 2. Monthly concentrations of BOD₅, COD_{Mn}, SO₄²⁻, and Cl⁻ in NR and ER

River	Conc. mg/L	Sampling time (month)											
		1	2	3	4	5	6	7	8	9	10	11	12
NR	BOD ₅	9.7	12.0	13.6	23.1	11	12.8	4.6	4.4	6.4	6.7	7.1	4.6
	COD _{Mn}	16.2	15.0	13.7	20.4	19.7	12.3	10	11.3	9.1	8.3	8.7	7.5
	SO ₄ ²⁻	73.4	62.6	51.7	79.8	332.5	125.9	71.5	64.5	45.6	316.3	64.2	53.4
	Cl ⁻	138.9	115.8	92.7	138.9	154.4	115.7	33.2	80.8	65.6	172.8	277.1	196.2
ER	BOD ₅	14.7	16.0	17.8	18.0	12.0	7.5	4.0	8.2	6.2	3.6	5.1	5.0
	COD _{Mn}	11.96	10.0	8.7	19.8	15.9	18.2	8.7	8.1	10.2	7.3	8.8	7.6
	SO ₄ ²⁻	69.6	60.3	51.1	143.2	114.2	168.6	73.98	54.7	52.0	98.5	66.3	60.5
	Cl ⁻	94.5	82.3	70.1	117.9	110.5	96.9	28.5	58.9	73.5	76.6	86.8	77.0

Dissolved N₂O concentration and emission flux

Overall, N₂O concentration ranged 16.12~143.09 nmol/L and averaged 226.27 ± 250.28 nmol/L (Fig. 3a, b). A clear seasonal variation in N₂O concentration was found in each river. Consistent seasonal trends were apparent between rivers. In general, the higher N₂O concentrations were observed in colder months. Difference in mean N₂O concentration was not significant between the two rivers ($P > 0.05$). During the sampling period, both rivers were oversaturated in N₂O with a range of 184~12084% (mean 2964%).

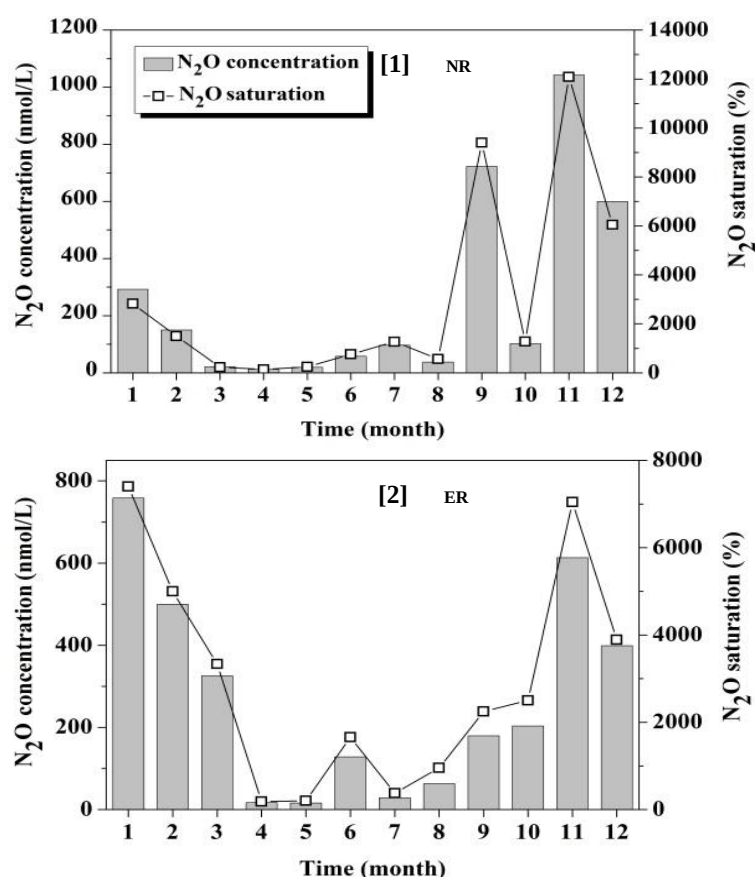


Figure 3. Seasonal variations in N₂O concentration and percentage saturation

This study indicates that NR and ER were net sources of N₂O across all the seasons sampled. N₂O emission fluxes also followed a distinct seasonal pattern ranging of 11.32~2920.38 µg N-N₂O/m²/h (mean 743.57 ± 831.78 µg N-N₂O/m²/h) (Fig. 4). Significantly lower N₂O emission fluxes were investigated in summer.

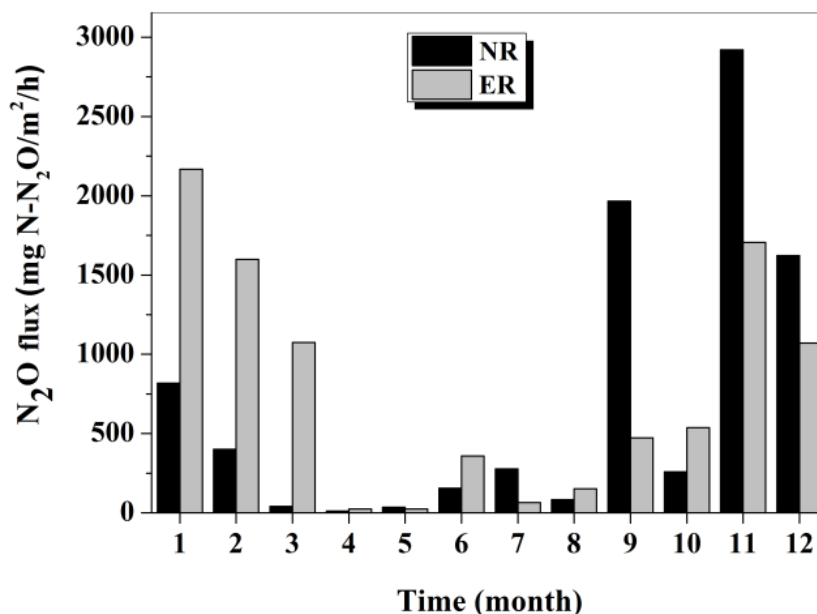


Figure 4. Seasonal variations in N₂O emission flux

Discussion

Compared to some literatures on the temporal and spatial variation of water pollution in the Zhegao River of Chaohu Lake basin (Chu et al., 2011; Yang et al., 2013), in which NH₄⁺, NO₃⁻, and TP showed an annual mean concentration of 1.13, 0.63, and 0.11 mg/L respectively. However, low NO₃⁻/Cl⁻ ratios (ranging 0.000~0.21, mean 0.04) were observed both in NR and ER in this study; this result further indicates that high riverine N concentrations in these rivers can be strongly attributed to the direct discharge of untreated sewage. Based on the measurements, the contribution of N₂O flux in colder seasons accounted for 90% of the annual budget, similar to results from two subtropical reservoirs (Liu et al., 2011, 2015), with lower fluxes of N₂O appearing in summer. However, different seasonal variation patterns on water surface N₂O emissions were also reported from the Three Gorges Reservoir in China (Zhu et al., 2013; Zhao et al., 2012). Some sewage-enriched rivers showed higher dissolved N₂O concentrations and were net atmospheric sources of N₂O. Xin'an Tang river (Taihu Lake basin of China) receiving high untreated sewage inputs indicated high N₂O concentration and emission flux with respective mean value of 0.48 µg N-N₂O/L and 56.1 µg N-N₂O/m²/h (Xia et al., 2013). The overall mean saturation and emission was 770% and 1.91 mg N-N₂O/m²/d in the Shanghai city river network (Yu et al., 2013), respectively. The urban rivers in Tianjin city (Haihe basin of China) showed high N₂O concentration and emission rate in winter with respective mean value of 88.9 nmol/L and 71.4 N-N₂O/m²/h (Hu et al., 2013; Liu et al., 2015). Thus, given the rapid progress of global urbanization, it is urgent to better understand the effect of urban rivers on global N₂O budget.

Seasonal variation in N₂O concentration and its potential control

Seasonal variations in N₂O concentration in two sampling rivers were observed in the study. Generally, the significantly higher N₂O concentration was observed in colder months. It has been reported that, seasonal patterns of trace gas concentration and emission in aquatic systems were governed by seasonal variability in temperatures affecting water availability, production of substrate precursors and microbial activity (Whalen, 2005; Quick et al., 2019). For example, water temperature positively correlated to N₂O saturation and explained 70% of the seasonal variance of N₂O saturation in a large and impounded river (Beaulieu et al., 2010). However, a negative correlation between water temperature and N₂O concentration was investigated in this study ($P = 0.03$) (Fig. 5). Some studies (Sun et al., 2013; Liu et al., 2015) also found a similar seasonal pattern in N₂O concentration and emission in the Yellow River estuary. It is indicated that this seasonal pattern of N₂O concentration in the NR and ER was mainly regulated by the inverse tendencies between temperature and riverine nutrient loadings during the study period. Small river discharge and high riverine nitrogen concentration was generally investigated during the cold seasons in this region. This combination of decreased water discharge and increased nutrient loadings is likely to have sustained high N₂O concentration in cold seasons. The correlation between NO₃⁻ and N₂O concentration was significant in NR but not significant in ER. These results suggested that N₂O may be produced by denitrification in NR while by coupled nitrification-denitrification in ER, which could be further proved by the significant negative correlation between DO and N₂O concentration in NR and significant positive correlation in ER. However, N₂O concentration was not significantly correlated with NH₄⁺ and NO₃⁻ based on the data collected.

It is suggested that none of the environmental variables stood out as a clearly superior predictor of N₂O when considered them alone, though several of them showed some predictive value with respect to dissolved N₂O concentration. Herein, a stepwise multiple regression that include DO, NH₄⁺, NO₃⁻, TP, BOD₅, COD_{Mn}, water temperature, and pH was conducted to assess predictors of N₂O concentration. The results showed that DO is a better predictor of N₂O in NR explaining 60% of variability in N₂O, indicating N₂O production was limited by DO concentration; while water temperature and NO₃⁻ are better predictors of N₂O in ER explaining 73% of variability in N₂O, indicating N₂O production was NO₃⁻ limited. Based on all of the observation data, water temperature and NO₃⁻ are better predictors of N₂O explaining 43% variability in N₂O. Other investigations also found similar relationships between NO₃⁻ and N₂O concentration in urban rivers (Wang et al., 2015; Quick et al., 2019). However, Yu et al. (2013) reported that N₂O production was greatly controlled by DO and NH₄⁺ level in some urban rivers. As discussed above, river N₂O may be produced by denitrification in NR while by coupled nitrification-denitrification in ER. Meanwhile, we thought that, high NH₄⁺ come from the decomposition of organic nitrogen in urban effluents in urban rivers, while NH₄⁺ cannot be oxidized to NO₃⁻ rapidly under hypoxic conditions. As a result, river N₂O production was NO₃⁻ limited based on the data collected.

Uncertainty of N₂O emission flux

There are many models for gas emission estimation. However, the overall accuracy of model-based gas estimation in rivers remains uncertain, since models were developed

in different settings and gas transfer coefficients (k) estimated with these models have not satisfied all field conditions (Kremer et al., 2003; Pauleta et al., 2019). In open waters, k is usually parameterized as a function of wind speed. It is reported that the primary driving mechanism that regulates k is presumed to be near-surface turbulence from low to moderate wind speeds; while at higher winds, bubble-mediated exchange produced by breaking waves may play significant roles on k (Borges et al., 2004). It is also reported that bottom-generated turbulence that is transported to the surface can significantly affect gas transfer especially in deep flowing waters (Nimmo-Smith et al., 1999; Zappa et al., 2003; Luo et al., 2019). Thus, choices of the models for estimation of k took a considerable bearing on the estimated gas emissions. Gas transfer velocity was directly measured in some studies to improve accuracy of estimating N₂O emission, as is however beyond this study.

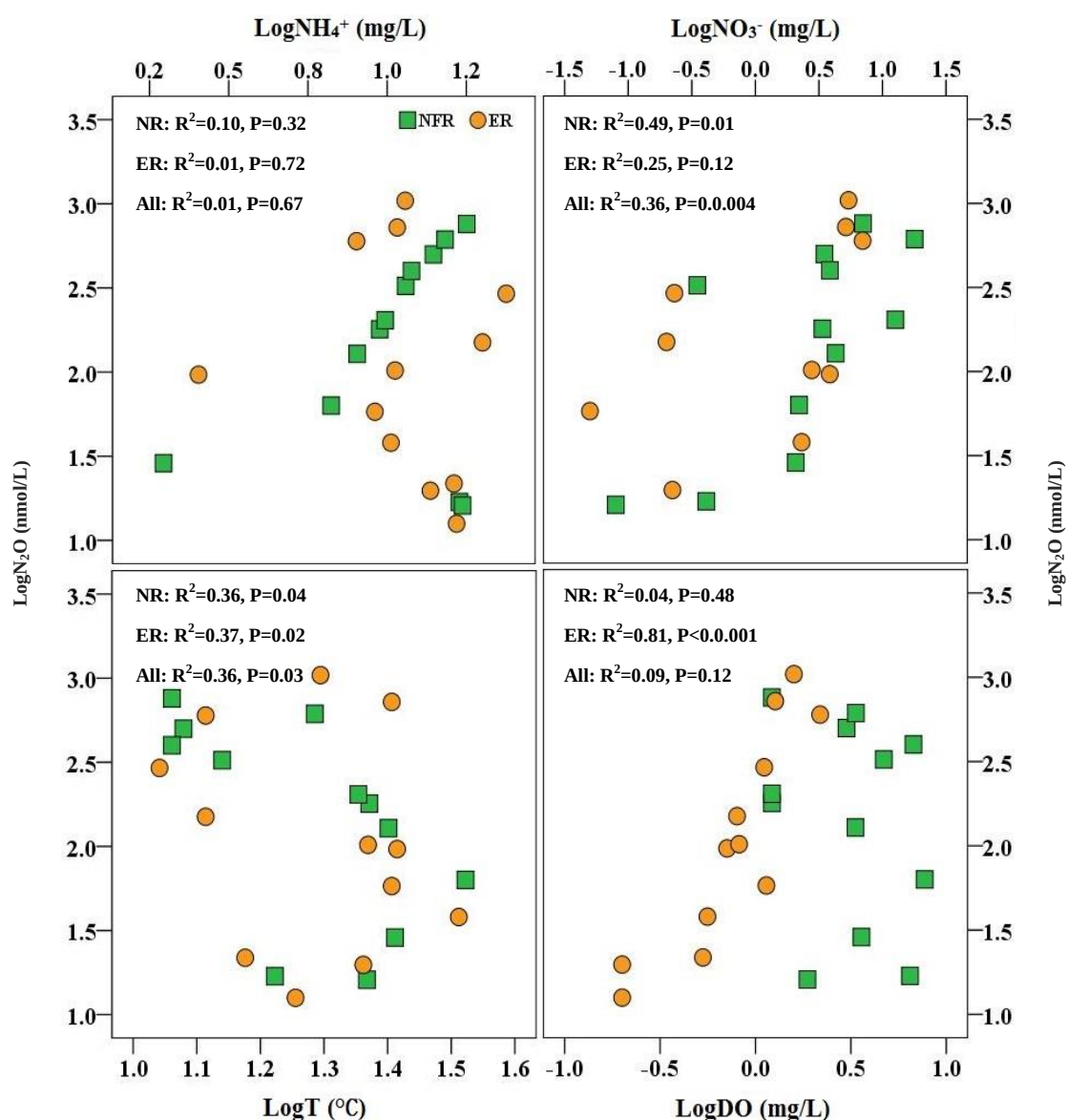


Figure 5. Simple linear regression analysis of normalized N₂O concentration with (a) normalized NH₄⁺, DO, (b) normalized NO₃⁻, (c) normalized water temperature (T), and (d) normalized DO for sampling rivers

Herein, 5 wind-based models (Liss and Merlivat, 1986; Wanninkhof, 1992; Raymond and Cole, 2001; Liu et al., 2015; Yang and Lei, 2018) and 2 wind-currents based models (Borges et al., 2004; Clough et al., 2007; Luo et al., 2019) were selected to compare the disparities in k_{N_2O} and eventually N₂O fluxes among models. The results showed wide disparities in gas transfer velocity estimates between different models. Overall, k_{N_2O} ranged 0.03~29.05 cm/h and averaged 4.26 ± 4.22 cm/h (Fig. 6). LM86a gave the lowest estimates while CL07 gave the highest estimation results. BO04 model expressed by Equation 2 gave an intermediate k_{N_2O} value (mean 4.77 ± 1.61 cm/h) relative to the other selected models. Generally, estimated k_{N_2O} using wind-based models indicated lower level than wind-current based model. Thus, studies that applied wind speed value only to estimate N₂O emissions in rivers may be grossly underestimating emissions and their contribution to the global budgets. The results also indicated that providing a range for the model-based N₂O emissions might be more reliable than providing a single flux value by using a single model.

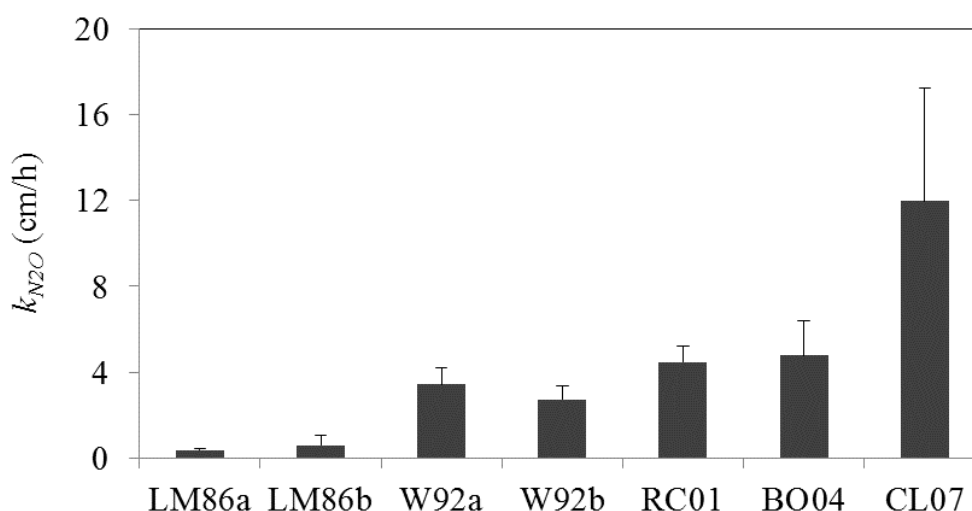


Figure 6. Comparison of gas transfer velocities estimated

Conclusions

Seasonal variation in N₂O concentrations and emissions of two urban rivers receiving sewage effluents in Chaohu Lake basin of China was investigated, to provide information on N₂O concentrations and emissions in the similar areas. The sampling rivers were oversaturated in N₂O and were net sources of atmospheric N₂O. Generally, significantly higher N₂O concentrations and emissions were observed during cold seasons. The simple linear regression analysis showed a negative correlation between N₂O concentration and water temperature based on the data collected, which may be regulated by the inverse tendencies between temperature and riverine N loadings during the study period. The results for the predicted production of riverine N₂O showed that DO is a better predictor of N₂O in NR explaining 60% of variability in N₂O, indicating N₂O production was limited by DO concentration; while water temperature and NO₃⁻ are better predictors of N₂O in ER explaining 73% of variability in N₂O, indicating N₂O production was NO₃⁻ limited. The riverine N₂O may be produced by denitrification in Nanfei River while by coupled nitrification-denitrification in Ershibu River.

Although further investigation is clearly needed to answer the question of how best to proceed before any unquestionable conclusion can be drawn, deriving quantitative estimates and the relative implications such as those presented in this study, is helpful to advance the policy debate. In the future, impacts of economic activities and land use on the concentration and emission of nitrous oxide in urban nitrogen-enriched rivers would be the crux in the relative study.

Acknowledgements. This study is supported by the Science & Technology Basic Resources Investigation Program of China (No. 2017FY101300) and Foundation of Ethnic Group Culture Research Base of Nanling Corridor, Key Research Institute of Humanities and Social Sciences in Guangxi General Universities (No. 2015KF03). We are also grateful for the help from Prof Kun Lei and Dr Sun Pu in the field sampling.

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