SEASONAL PATTERN OF N_2O CONCENTRATIONS AND EMISSIONS IN THE SEWAGE-ENRICHED RIVERS: CASE OF CHAOHU LAKE BASIN IN SOUTHEAST CHINA

YANG, L.B.[1,2] – LI, F.[2*]

[1]*River and Coastal Environment Research Center, Chinese Research Academy of Environmental Sciences, Beijing 100012, China*

[2]*Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101, China*

Both authors contributed equally to this work, in no particular order.

**Corresponding author: LI, F.*
e-mail: lifcas@gmail.com

(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 (N_2O) concentrations, to improve the information of N_2O concentrations and emissions in the similar areas. The results indicate that N_2O concentrations ranged 16.12~1043.09 nmol/L and averaged 266.27 ± 250.28 nmol/L during the sampling period. N_2O was oversaturated in both rivers ranging 184~12084% (mean 2964%). The significantly higher level of N_2O concentrations and emissions were observed in cold months. It is indicated that the two rivers were net sources of atmospheric N_2O. N_2O emissions ranged 11.32~2920.38 μg $N\text{-}N_2O/m^2/h$ with an overall mean value of 743.57 ± 831.78 μg $N\text{-}N_2O/m^2/h$. A significant negative correlation exists between N_2O concentration and water temperature, which may be regulated by inverse tendencies between temperature and riverine nutrient loadings. Dissolved Oxygen (DO) is a predictor of N_2O in Nanfei River explaining 60% of variability in N_2O; while water temperature and NO_3^- are better predictors of N_2O in Ershibu River explaining 73% of variability in N_2O. The riverine N_2O 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 (N_2O) 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 N_2O 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 N_2O 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 N_2O on the global scale, equivalent to 10% of the anthropogenic N_2O 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 N_2O from different sources as accurate information is required to determine the contribution of N_2O to global greenhouse gas fluxes (Khalil et al., 2002; Yang and Lei, 2018).

Among the many natural and anthropogenic N_2O sources, most are biological ones (Short et al., 2013). In aquaculture systems, N_2O can be produced by denitrification under anaerobic conditions, where NO_3^- was converted to N_2O and dinitrogen (N_2)

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1704_79737985

(Öquist et al., 2004). Under oxic conditions, N_2O is also produced as a by-product of nitrification where ammonium (NH_4^+) was oxidized to nitrite (NO_2^-), and subsequently to NO_3^- (Stein and Yung, 2003). Natural rivers have shown large temporal and spatial variations in their N_2O 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 N_2O 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 N_2O emission from denitrification and nitrification. Controlling factors related to N_2O 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 N_2O concentration in rivers.

Emissions of N_2O 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 N_2O emissions from terrestrial ecosystems; however, emissions of N_2O from rivers and streams have received much less attention and remain a major source of uncertainty in the global N_2O 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 N_2O 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 N_2O emissions. Therefore, this study aimed to determine: (1) the presence and extent of seasonal variations in river water chemistry, dissolved N_2O concentration and emissions in sewage-enriched rivers in the Chaohu Lake region; (2) the potential factors that regulate the seasonal N_2O 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

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1704_79737985

(*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 N_2O 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

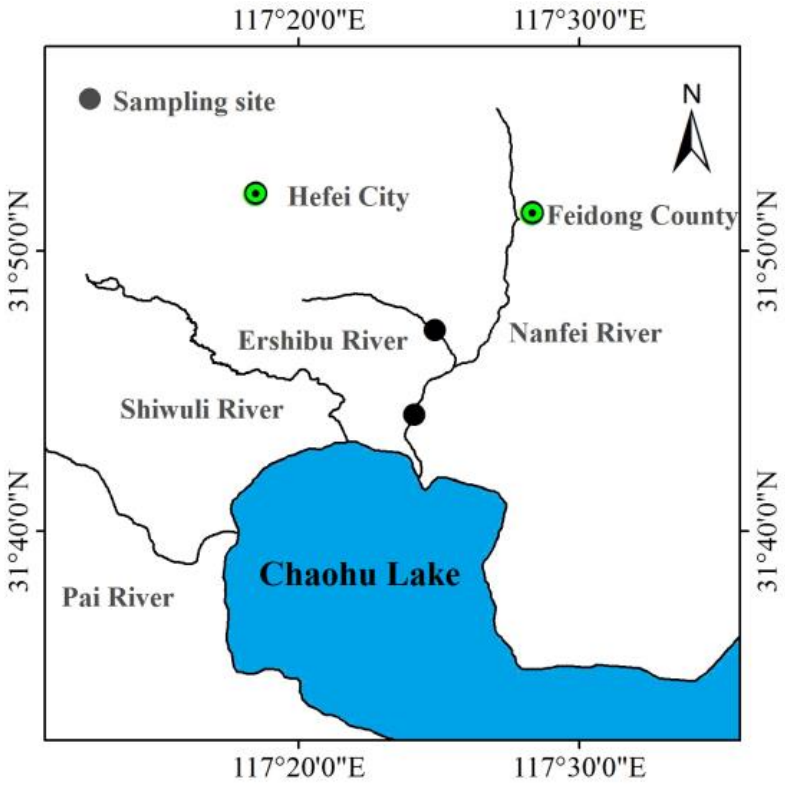

Figure 1. *The location of the sampling rivers and sampling sites*

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 NH_4^+, NO_3^-, TP, BOD_5, COD_{Mn}, SO_4^{2-}, and Cl^-. Dissolved oxygen (DO), pH, and water temperature were measured *in situ* using a portable meter (HQ30D, USA). Samples for dissolved N_2O 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.

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1704_79737985

The respective concentration of NH_4^+, NO_3^-, TP, BOD_5, COD_{Mn}, SO_4^{2-}, 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 N_2O 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 N_2 (purity > 99.999%) was injected into the serum bottle using an airtight syringe and a 20-ml water sample was displaced. Bottle headspace N_2O 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 N_2O concentrations (C_w) in water samples were calculated (Johnson et al., 1990; Yang and Lei, 2018). The equilibrium concentration (C_e) of N_2O in river water with atmosphere was calculated using Henry's first law. Dissolved N_2O saturation, expressed in %, was calculated by comparing C_w and C_e.

N_2O emission flux

N_2O 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 N_2O emission flux (μg $N\text{-}N_2O/m^2/h$); C_w and C_e is the measured and equilibrium concentration of N_2O (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; Sc is the Schmidt number for N_2O 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

NH_4^+ and NO_3^- concentrations varied considerably over the sampling time, ranging 1.97~23.75 (mean12.24 ± 5.13) and 0.05~6.98 (mean3.54 ± 4.45) mg/L (*Fig. 2a, b*), respectively. NH_4^+ and NO_3^- concentrations indicated a generally higher level in cold months ($P < 0.001$). Difference in mean NH_4^+ and NO_3^- 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 NH_4^+, 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*).

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1704_79737985

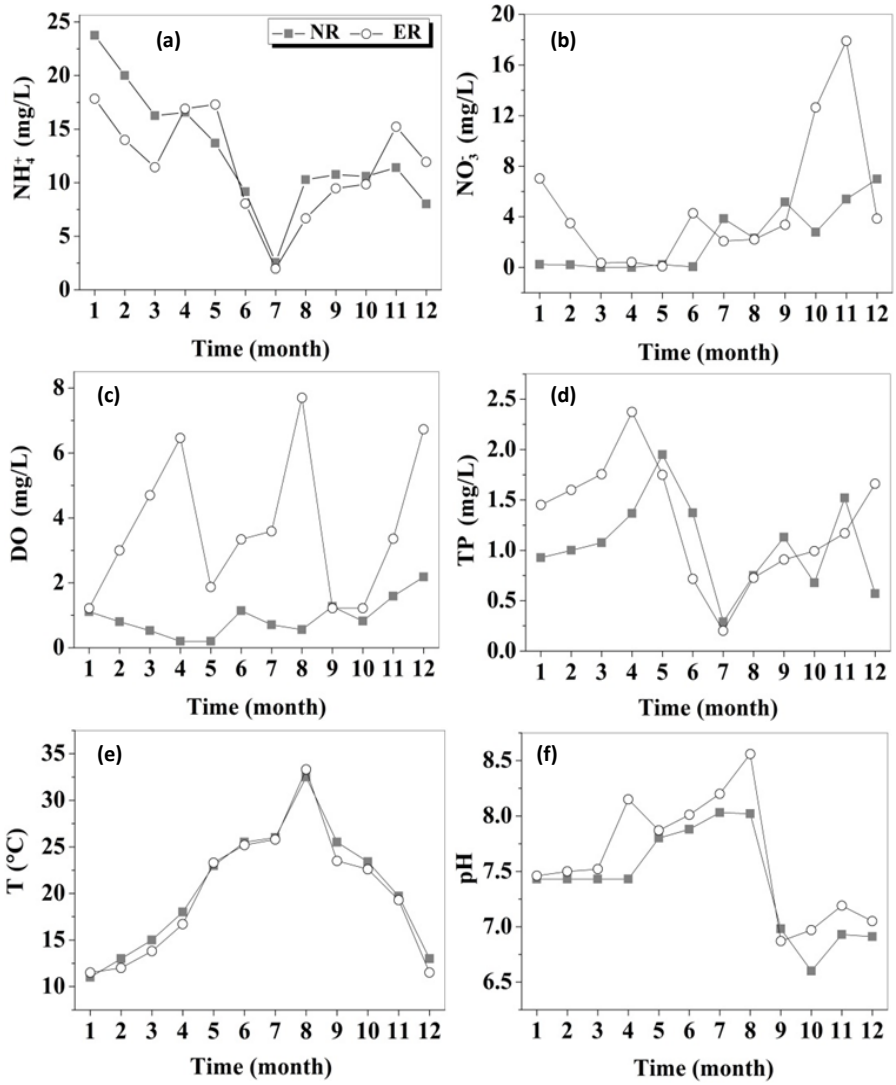

Figure 2. *Seasonal variations in NH_4^+, NO_3^-, DO, TP, water temperature (T), and pH value of Nanfei and Ershibu River*

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.

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1704_79737985

Table 2. *Monthly concentrations of BOD_5, COD_{Mn}, SO_4^{2-}, 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 N_2O concentration and emission flux

Overall, N_2O concentration ranged 16.12~143.09 nmol/L and averaged 226.27 ± 250.28 nmol/L (*Fig. 3a, b*). A clear seasonal variation in N_2O concentration was found in each river. Consistent seasonal trends were apparent between rivers. In general, the higher N_2O concentrations were observed in colder months. Difference in mean N_2O concentration was not significant between the two rivers ($P > 0.05$). During the sampling period, both rivers were oversaturated in N_2O with a range of 184~12084% (mean 2964%).

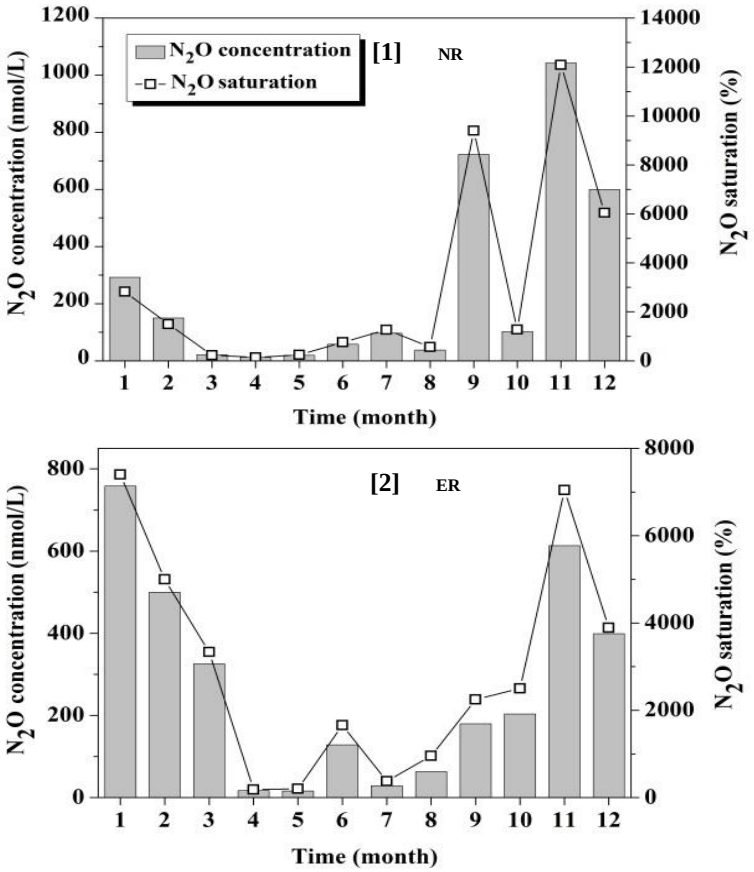

Figure 3. *Seasonal variations in N_2O concentration and percentage saturation*

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1704_79737985

This study indicates that NR and ER were net sources of N_2O across all the seasons sampled. N_2O emission fluxes also followed a distinct seasonal patter ranging of 11.32~2920.38 μg N-N_2O/m^2/h (mean 743.57 ± 831.78 μg N-N_2O/m^2/h) (*Fig. 4*). Significantly lower N_2O emission fluxes were investigated in summer.

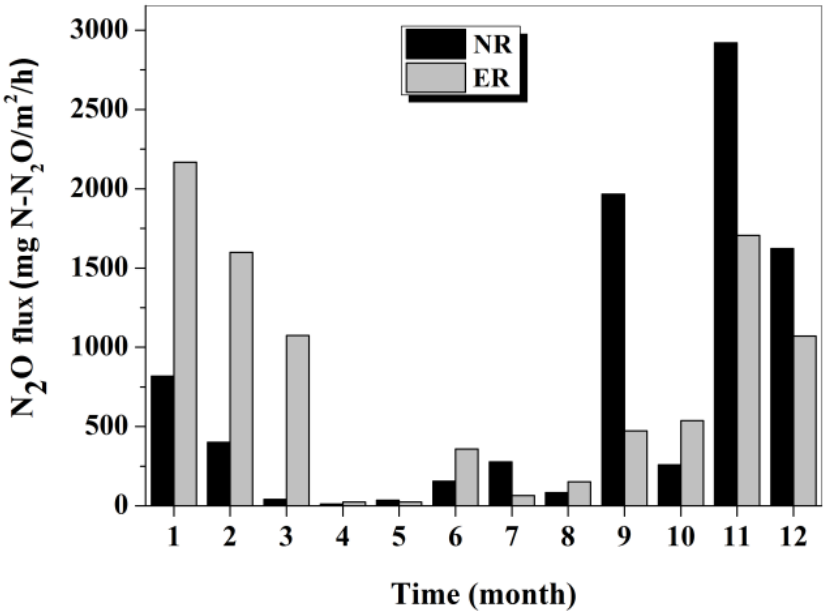

Figure 4. *Seasonal variations in N_2O emission flux*

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 NH_4^+, NO_3^-, and TP showed an annual mean concentration of 1.13, 0.63, and 0.11 mg/L respectively. However, low NO_3^-/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 N_2O 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 N_2O appearing in summer. However, different seasonal variation patterns on water surface N_2O 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 N_2O concentrations and were net atmospheric sources of N_2O. Xin'an Tang river (Taihu Lake basin of China) receiving high untreated sewage inputs indicated high N_2O concentration and emission flux with respective mean value of 0.48 μg N-N_2O/L and 56.1 μg N-N_2O/m^2/h (Xia et al., 2013). The overall mean saturation and emission was 770% and 1.91 mg N-N_2O/m^2/d in the Shanghai city river network (Yu et al., 2013), respectively. The urban rivers in Tianjin city (Haihe basin of China) showed high N_2O concentration and emission rate in winter with respective mean value of 88.9 nmol/L and 71.4 N-N_2O/m^2/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 N_2O budget.

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1704_79737985

Seasonal variation in N_2O concentration and its potential control

Seasonal variations in N_2O concentration in two sampling rivers were observed in the study. Generally, the significantly higher N_2O 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 N_2O saturation and explained 70% of the seasonal variance of N_2O saturation in a large and impounded river (Beaulieu et al., 2010). However, a negative correlation between water temperature and N_2O 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 N_2O concentration and emission in the Yellow River estuary. It is indicated that this seasonal pattern of N_2O 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 N_2O concentration in cold seasons. The correlation between NO_3^- and N_2O concentration was significant in NR but not significant in ER. These results suggested that N_2O 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 N_2O concentration in NR and significant positive correlation in ER. However, N_2O concentration was not significantly correlated with NH_4^+ and NO_3^- based on the data collected.

It is suggested that none of the environmental variables stood out as a clearly superior predictor of N_2O when considered them alone, though several of them showed some predictive value with respect to dissolved N_2O concentration. Herein, a stepwise multiple regression that include DO, NH_4^+, NO_3^-, TP, BOD_5, COD_{Mn}, water temperature, and pH was conducted to assess predictors of N_2O concentration. The results showed that DO is a better predictor of N_2O in NR explaining 60% of variability in N_2O, indicating N_2O production was limited by DO concentration; while water temperature and NO_3^- are better predictors of N_2O in ER explaining 73% of variability in N_2O, indicating N_2O production was NO_3^- limited. Based on all of the observation data, water temperature and NO_3^- are better predictors of N_2O explaining 43% variability in N_2O. Other investigations also found similar relationships between NO_3^- and N_2O concentration in urban rivers (Wang et al., 2015; Quick et al., 2019). However, Yu et al. (2013) reported that N_2O production was greatly controlled by DO and NH_4^+ level in some urban rivers. As discussed above, river N_2O may be produced by denitrification in NR while by coupled nitrification-denitrification in ER. Meanwhile, we thought that, high NH_4^+ come from the decomposition of organic nitrogen in urban effluents in urban rivers, while NH_4^+ cannot be oxide to NO_3^- rapidly under hypoxic conditions. As a result, river N_2O production was NO_3^- limited based on the data collected.

Uncertainty of N_2O 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

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1704_79737985

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 N_2O emission, as is however beyond this study.

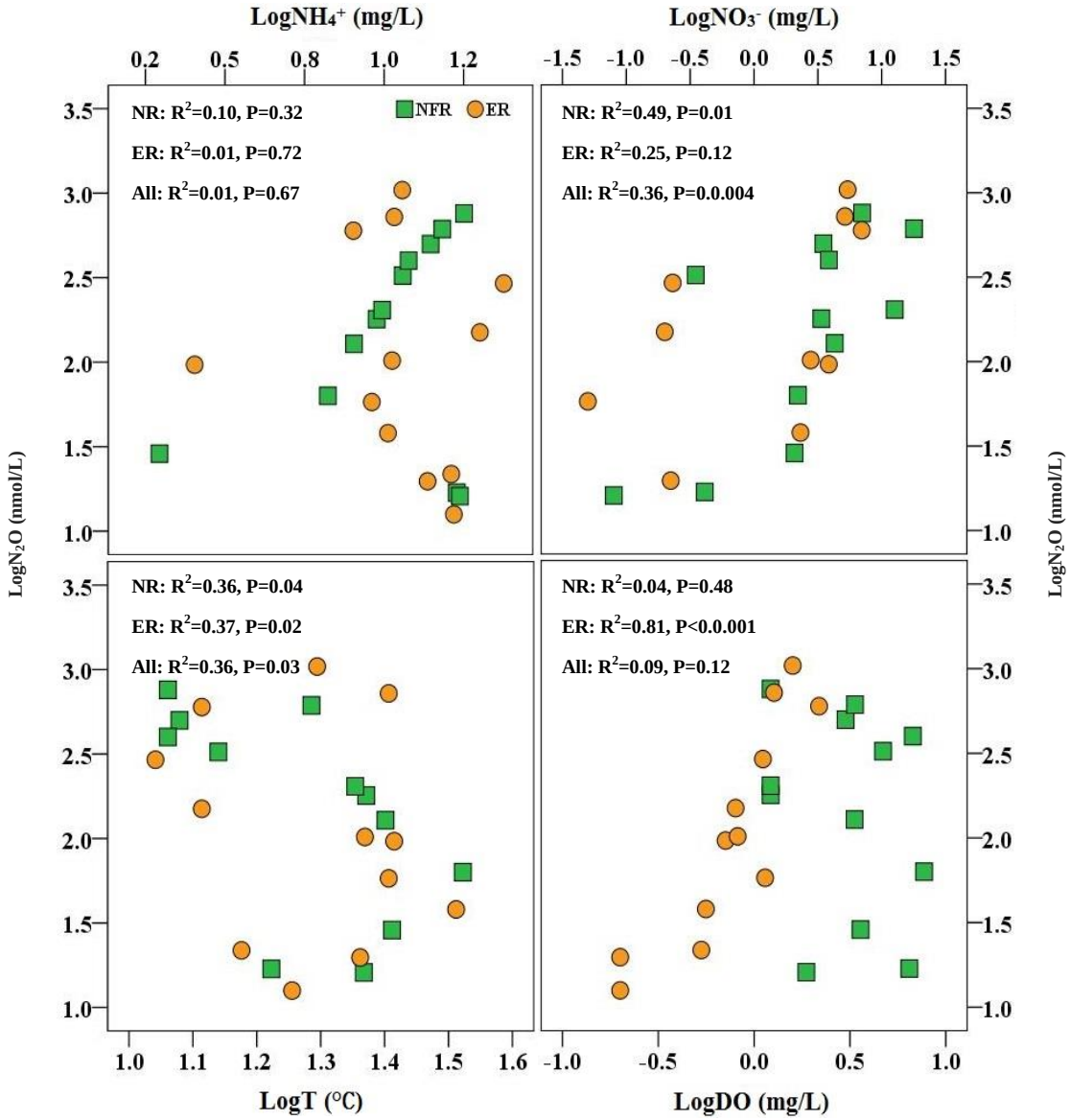

Figure 5. *Simple linear regression analysis of normalized N_2O concentration with (a) normalized NH_4^+, DO, (b) normalized NO_3^-, (c) normalized water temperature (T), and (d) normalized DO for sampling rivers*

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1704_79737985

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_{N2O} and eventually N_2O fluxes among models. The results showed wide disparities in gas transfer velocity estimates between different models. Overall, k_{N2O} 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_{N2O} value (mean 4.77 ± 1.61 cm/h) relative to the other selected models. Generally, estimated k_{N2O} using wind-based models indicated lower level than wind-current based model. Thus, studies that applied wind speed value only to estimate N_2O 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 N_2O emissions might be more reliable than providing a single flux value by using a single model.

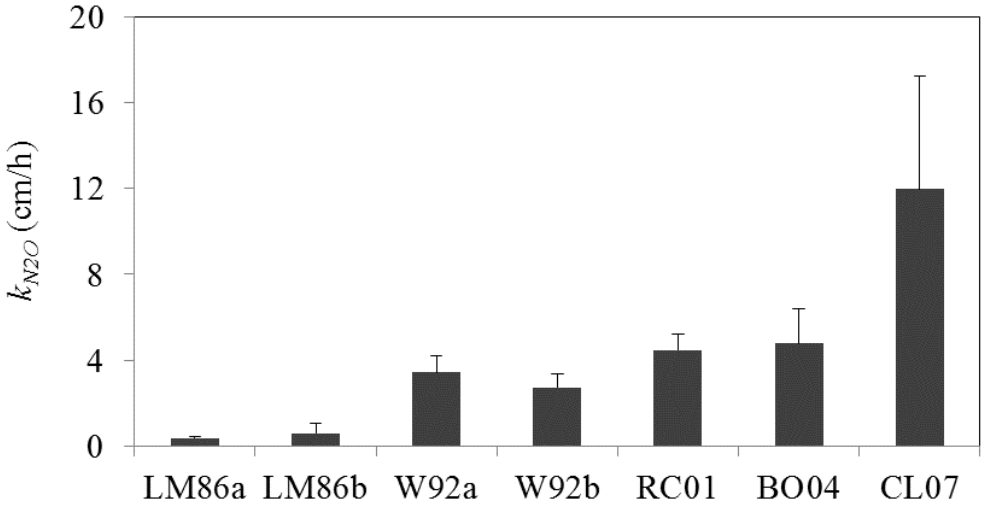

Figure 6. *Comparison of gas transfer velocities estimated*

Conclusions

Seasonal variation in N_2O concentrations and emissions of two urban rivers receiving sewage effluents in Chaohu Lake basin of China was investigated, to provide information on N_2O concentrations and emissions in the similar areas. The sampling rivers were oversaturated in N_2O and were net sources of atmospheric N_2O. Generally, significantly higher N_2O concentrations and emissions were observed during cold seasons. The simple linear regression analysis showed a negative correlation between N_2O 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 N_2O showed that DO is a better predictor of N_2O in NR explaining 60% of variability in N_2O, indicating N_2O production was limited by DO concentration; while water temperature and NO_3^- are better predictors of N_2O in ER explaining 73% of variability in N_2O, indicating N_2O production was NO_3^- limited. The riverine N_2O may be produced by denitrification in Nanfei River while by coupled nitrification-denitrification in Ershibu River.

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1704_79737985

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.

REFERENCES

[1] Alexander, R. B., Smith, R. A., Schwarz, G. E. (2000): Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. – Nature 403: 758-761.
[2] Bansal, S., Chakraborty, M., Katyal, D., Garg, J. K. (2015): Methane flux from a subtropical reservoir located in the floodplains of River Yamuna, India. – Applied Ecology and Environmental Research 13(2). 597-613.
[3] Beaulieu, J. J., Shuster, W. D., Rebholz, J. A. (2010): Nitrous oxide emissions from a large, impounded river: the Ohio River. – Environmental Science and Technology 44: 7527-7533.
[4] Beaulieu, J. J., Tank, J. L., Hamilton, S. K., Wollheim, W. M., Hall, R. O, Mulholland, P. J., Peterson, B. J., Ashkenas, L. R., Cooper, L. W., Dahm, C. N. (2011): Nitrous oxide emission from denitrification in stream and river networks. – Proceedings of the National Academy of Sciences 108: 214-219.
[5] Borges, A. V., Vanderborght, J. P., Schiettecatte, L. S., Gazeau, F., Ferrón-Smith, S., Delille, B., Frankignoulle, M. (2004): Variability of the gas transfer velocities of CO_2 in a macrotidal estuary (the Scheldt). – Estuaries 27: 593-603.
[6] Bouwman, A. F. (1995): Compilation of a global inventory of emissions of nitrous oxide. – PhD thesis, Agricultural University, Wageningen, Netherlands.
[7] Chu, Y., Zhu, J., Xia, S. X., Ma, Y. H., Jiang, L. T., Li, Y., Li, X. C. (2011): Temporal and spatial variation of water pollution in Zhegao River of Chao Lake Basin. – Journal of Soil and Water Conservation 25(4): 243-248.
[8] Clough, T. J., Buckthought, L. E., Kelliher, F. M., Sherlock, R. R. (2007): Diurnal fluctuations of dissolved nitrous oxide (N_2O) concentrations and estimates of N_2O emissions from a spring-fed river: Implications for IPCC methodology. – Global Change Biology 13: 1016-1027.
[9] Holland, E. A., Braswell, B. H., Sulzman, J., Lamarque, J. F. (2005): Nitrogen deposition onto the United States and Western Europe: synthesis of observations and models. – Journal of Applied Ecology 15: 38-57.
[10] Hu, B. B., Tan, Y. J., Wang, D. Q., Deng, H. G.; Lin, Y. J., Yu, Z. J., Chen, Z. L. (2013): Methane and nitrous oxide dissolved concentration and emission flux of Plain River network in winter. – Science China Chemistry 43(7): 919-929.
[11] Huttunen, J. T., Väisänen, T. S., Hellsten, S. K. (2002): Fluxes of CH_4, CO_2, and N_2O in hydroelectric reservoirs Lokka and Porttipahta in the northern boreal zone in Finland. – Global Biogeochemical Cycles 16(1): 1-17.
[12] Johnson, K. M., Hughes, J. E., Donaghay, P. L. (1990): Bottle-calibration static head space method for the determination of methane dissolved in seawater. – Analytical Chemistry 62(21): 2408-2412.

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1704_79737985

[13] Khalil, M. A. K., Rasmussen, A., Shearer, M. J. (2002): Atmospheric nitrous oxide: patterns of global change during recent decades and centuries. – Chemosphere 47: 807-821.
[14] Kremer, J. N., Nixon, S. W., Buckley, B., Roques, P. (2003): Technique note: conditions for using the floating chamber method to estimate air-water gas exchange. – Estuaries 26(4): 985-990.
[15] Liss, P. S., Merlivat, L. (1986): Air-Sea Gas Exchange Rates: Introduction and Synthesis. – In: Buat-Ménard, P. (ed.) The Role of Air-Sea Exchange in Geochemical Cycling. Springer, Dordrecht, the Netherlands.
[16] Liu, X. L., Liu, C. Q., Li, S. L., Wang, F. S., Wang, B. L., Wang, Z. L. (2011): Spatial-temporal variations of nitrous oxide (N_2O) emissions from two reservoirs in SW China. – Atmospheric Environment 45: 5458-5468.
[17] Liu, X. L., Bai, L., Wang, Z. L., Li, J., Yue, F. J., Li, S. L. (2015): Nitrous oxide emissions from river network with variable nitrogen loading in Tianjin, China. – Journal of Geochemical Exploration 157: 153-161.
[18] Luo, Z. B., Lam, S. K., Fu, H., Hu, S. Y., Chen, D. L. (2019): Temporal and spatial evolution of nitrous oxide emissions in China: assessment, strategy and recommendation. – Journal of Cleaner Production 223: 360-367.
[19] Nimmo-Smith, W. A. M., Thorpe, S. A., Graham, A. (1999): Surface effects of bottom-generated turbulence in a shallow tidal sea. – Nature 400: 251-254.
[20] Öquist, M. G., Nilsson, M., Sörensson, F., Kasimir-Klemedtsson, A., Persson, T., Weslien, P., Klemedtsson, L. (2004): Nitrous oxide production in a forest soil at low temperatures-processes and environmental controls. – FEMS Microbiology Ecology 49: 371-378.
[21] Pauleta, S. R., Carepo, M. S. P., Moura, I. (2019): Source and reduction of nitrous oxide, – Coordination Chemistry Reviews 387: 436-449.
[22] Quick, A. M., Reeder, W. J., Farrell, T. B., Tonina, D., Feris, K. P., Benner, S. G. (2019): Nitrous oxide from streams and rivers: a review of primary biogeochemical pathways and environmental variables. – Earth-Science Reviews 191: 224-262.
[23] Ravishankara, A. R., Daniel, J. S., Portmann, R. W. (2009): Nitrous oxide (N_2O): The dominant ozone-depleting sub-stance emitted in the 21st century. – Science 326(5949): 123-125.
[24] Raymond, P. A., Cole, J. J. (2001): Gas exchange in rivers and estuaries: choosing a gas transfer velocity. – Estuaries 24: 312-317.
[25] Richey, J. E., Melack, J. M., Aufdenkampe, A. K., Ballester, V. M., Hess, L. L. (2002): Outgassing from Amazonian rivers and wetlands as a large tropical source of atmospheric CO_2. – Nature 416: 617-620.
[26] Short, M. D., Peters, G. M., Peirson, W. L., Ashbolt, N. J. (2013): Marine nitrous oxide emissions: an unknown liability for the international water sector. – Environmental science & policy 33: 209-221.
[27] Stein, L. Y., Yung, Y. L. (2003): Production, isotopic composition, and atmospheric fate of biologically produced nitrous oxide. – Annual Review of Earth and Planetary Sciences 31: 329-356.
[28] Sun, Z. G., Wang, L. L., Tian, H. Q., Jiang, H. H., Mou, X. J., Sun, W. L. (2013): Fluxes of nitrous oxide and methane in different coastal Suaeda salsa marshes of the Yellow River estuary, China. – Chemosphere 90: 856-865.
[29] Wang, D. Q., Chen, Z. L., Wang, J., Xu, S. Y., Yang, H. X., Chen, H., Yang, L. Y., Hu, L. Z. (2007): Summer-time denitrification and nitrous oxide exchange in the intertidal zone of the Yangtze estuary. – Estuarine Coastal and Shelf Science 73: 43-53.
[30] Wang, J. N., Chen, N. W., Yan, W. J., Wang, B., Yang, L. B. (2015): Effect of dissolved oxygen and nitrogen on emission of N_2O from rivers in China. – Atmospheric Environment 103: 347-356.

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1704_79737985

[31] Wanninkhof, R. (1992): Relationship between wind speed and gas exchange over the ocean. – Journal of Geophysical Research 97(C5): 7373-7382.
[32] Whalen, S. C. (2005): Biogeochemistry of methane exchange between natural wetlands and the atmosphere. – Environmental Engineering Science 22: 73-94.
[33] Wilcock, R. J., Nagels, J. W., Mcbride, G. B., Collier, K. J., Wilson, B. T., Huser, B. A. (1998): Characterization of lowland streams using a single-station diurnal curve analysis model with continuous monitoring data for dissolved oxygen and temperature. – New Zealand Journal of Marine and Freshwater Research 32: 67-79.
[34] Wollheim, W. M., Vorosmarty, C. J., Peterson, B. J., Seitzinger, S. P., Hopkinson, C. S. (2006): Relationship between river size and nutrient removal. – Geophysical Research Letters 33: L06410.
[35] Wójcik-Gront, E. (2015): Territorial analysis of agricultural greenhouse gas emission in Poland. – Applied Ecology and Environmental Research 13(2): 417-425.
[36] Xia, Y. Q., Li, Y. F., Li, X. B., Guo, M., She, D. L., Yan, X. Y. (2013): Diurnal pattern in nitrous oxide emissions from a sewage-enriched river. – Chemosphere 92: 421-428.
[37] Yang, H. X., Wang, D. Q., Chen, Z. L., Xu, S. Y. (2006): Elementary research on greenhouse gas emissions in Chongming east intertidal flat of the Changjiang estuary. – Marine Environmental Research 25: 20-23.
[38] Yang, L. B., Lei, K. (2018): Effects of land use on the concentration and emission of nitrous oxide in nitrogen-enriched rivers. – Environmental Pollution 238: 379-388.
[39] Yang, L. B., Lei, K, Meng, W., Fu, G., Yan, W. J. (2013): Temporal and spatial changes in nutrients and chlorophyll-a in a shallow lake, Lake Chaohu, China: an 11-year investigation. – Journal of Environmental Sciences 25(6): 1117-1123.
[40] Yu, J. Z., Deng, H. G., Wang, D. Q., Ye, M. W., Tan, Y. J., Li, Y. J., Chen, Z. L., Xu, S. Y. (2013): Nitrous oxide emissions in the Shanghai river network: implications for the effects of urban sewage and IPCC methodology. – Global Change Biology 19: 2999-3010.
[41] Zappa, C. J., Raymond, P. A., Terray, E. A., Mcgillis, W. R. (2003): Variation in surface turbulence and the gas transfer velocity over a tidal cycle in a macro-tidal estuary. – Estuaries 26(6): 1401-1415.
[42] Zhao, Y., Wu, B. F., Zeng, Y. (2012): Spatial and temporal aspects of greenhouse gas emissions from Three Gorges Reservoir, China. – Biogeosciences Discuss 9: 14503-14535.
[43] Zhu, D., Chen, H., Yuan, X. Z., Wu, N., Gao, Y. H., Wu, Y., Zhang, Y. M., Peng, C. H., Zhu, Q. A., Yang, G., Wu, J. H. (2013): Nitrous oxide emissions from the surface of the Three Gorges Reservoir. – Ecological Engineering 60: 150-154.

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1704_79737985