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Nitrous oxide emissions from river network with variable nitrogen loading in Tianjin, China

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ABSTRACT

Surface waters impacted by urbanization and anthropogenic activities, especially streams and rivers, can be a significant source of nitrous oxide (N_2O), but little is known about how the nitrogen enrichment in urban and rural rivers will increase the N_2O emission. Tianjin surface waters including urban and rural river network and lakes were sampled and analyzed for N loadings and N_2O concentrations. The study showed that eutrophied urban rivers in Tianjin were oversaturated with respect to N_2O with a saturation ranging from 252% to 3116% and acted as source of N_2O whereas rural rivers were generally undersaturated, with the a saturation ranging from 3% to 354% and acted as a sink of N_2O. Mean values of estimated N_2O fluxes in urban and rural rivers were 2.10 μmol m^{-2} d^{-1} and −0.24 μmol m^{-2} d^{-1}, respectively. Anthropogenic inorganic N load plays primary control on the distribution of N_2O saturation in heavily eutrophied rivers and estuaries, but N_2O emission did not increase as much as expected in response to high N inputs, especially in rural rivers. Whereas nitrification might be the main process responsible for N_2O production in urban lakes and rivers in Tianjin, both nitrification and denitrification could contribute to N_2O production in nearby estuaries. In comparison, denitrification is a N_2O sink in rural rivers of Tianjin. The annual emission from the river network of Tianjin was estimated to be 5.78×10^3 kg N-N_2O, a moderate emission when compared with worldwide rivers, but N_2O emission in urban rivers and lakes indicated that globally aquatic N_2O emission rate and fluxes were probably underestimated in the 2007 IPCC report. More efforts should be paid to globally quantified N_2O in eutrophied urban rivers for better assessment of N_2O emission in riverine systems.

1. Introduction

Nitrous oxide (N_2O) continuously attracts considerable attention as an atmospheric gas that contributes to global warming and ozone depletion. Its emissions are expected to remain the largest ones throughout the 21st century (Ravishankara et al., 2009). In addition, N_2O is the third most important natural long-lived greenhouse gas, after CO_2 and CH_4, and its global warming potential (GWP) is 296 times that of CO_2 (IPCC, 2007). Atmospheric N_2O has been increasing steadily over the past century by approximately 0.25 ± 0.05% yr^{-1} and aquatic system is an important source which contributes between 25% and 30% of the total global N_2O emission (Ravishankara et al., 2009).

Anthropogenic nitrogen (N) loading to river networks through the increasing application of N fertilizers is currently an important source of N_2O via microbial denitrification and nitrification. Rivers, and river dominated estuaries, which receive about 20% of this N fertilizer, globally (Cole and Caraco, 2001) may be especially important hot spots for the production of N_2O. Recently, it has been estimated that the enhancement of riverine N_2O emission by anthropogenic input of dissolved inorganic N into rivers reached 0.9 Tg yr^{-1} for global river systems (Rosamond et al., 2012). Based on a global land use model, Seitzinger and Kroeze estimate that global N_2O production from rivers alone could be as large as 1.8 Tg N y^{-1} or more than 20%–30% of the anthropogenic production of N_2O on land (Seitzinger and Kroeze, 1998; Seitzinger et al., 2000). For a number of reasons this estimate has a large uncertainty, but the model assumes that there is a direct connection between the input of DIN to rivers and the output of N_2O gas. However, a recent study indicated that microbial N transformations, including denitrification and nitrification, converted at least 0.68 Tg y^{-1} of anthropogenic N inputs to N_2O in river networks, which is three times more than estimated by the Intergovernmental Panel on Climate Change reported in 2007 (Beaulieu et al., 2011).

Urbanization and anthropogenic impacted surface waters, particularly in streams and rivers, can be a significant source of nitrous oxide (N_2O). N_2O saturation and emission from Shanghai river network were 770% and 1.91 mg N_2O-N m^{-2} d^{-1}, respectively (Yu et al., 2013) and the Hudson River contributes by 0.056 g of N_2O-N m^{-2} to the atmosphere annually (Cole and Caraco, 2001). But little is known about how the nitrogen enrichment in urban and rural rivers will increase the N_2O emission. As reported and confirmed by lots of recent studies

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in surface waters worldwide, NO_3^- is supposed to dominate N form and positively contribute to N_2O production (Clough et al., 2007; Hinshaw and Dahlgren, 2013; Li et al., 2010). Calculated N_2O emissions from China are globally significant, accounting for over 90% of those in the Pacific Basin (Seitzinger and Kroeze, 1998). While the potential for rivers to contribute for substantial N_2O emission to the atmosphere is high, there have been relatively few direct studies assessing the production and emission of N_2O to the atmosphere in eutrophied rivers in China, especially in large urban rivers. In addition, the effects of anthropogenic nutrient inputs on riverine N_2O emissions are not well understood (Hinshaw and Dahlgren, 2013; Yu et al., 2013). Therefore, this study was conducted (1) to examine the dissolved N_2O saturation in the Tianjin river networks and lakes and estuaries, then to confirm how N loadings affect the N_2O saturation; (2) to reveal N_2O production mechanisms under eutrophied aquatic environment; and (3) to assess N_2O emission fluxes in urban rivers and rural rivers, then try to do efforts on evaluating globally aquatic N_2O emission and its potential.

2. Materials and methods

2.1. Study site

Tianjin, one of the most populated coastal metropolises in the world (nearly 15 million people), is surrounded by Bohai Sea on the east and Yanshan mountain to the north. Tianjin municipality is divided into urban area and rural area by loop highway as showed in Fig. 1. The studied region is subject to a warm temperate semi-humid monsoon climate and has a typical East Asia monsoon climate with an average annual temperature of 14.8 °C. The multi-year average annual rainfall is 520–660 mm, with 75% of the total precipitation occurring in June, July and August. Major rivers in the study area include the Haihe River, Yongdingxin River, Caobaixin River, and the Jiyun River. The Haihe River is fed by five major rivers (Beiyun River, Yongding River, Daqing River, Ziya River, Nanyun River) that flow into Tianjin from the north, west, and south and then out to the Bohai Sea. Another three rivers in the vicinity of the city (Yongdingxin River, Caobaixin River, Jiyun River) also flow into the Bohai Sea. The surface water is major water sources for the city. The water resources in Tianjin are limited. As the city continues to develop, protection and management of water resources will become increasingly important.

2.2. Sampling

Sampling sites were set up along the river network and samples were collected in July 2011 throughout the Tianjin municipality (see Fig. 1). To investigate spatial variation of N_2O in study district, a wide range of measurements were carried out at 46 sites for different types of waters including 10 sampling sites for lakes, 22 sampling sites for rural rivers, 11 sampling sites for urban rivers, and 3 sampling sites for estuaries. For better understanding the emission of N_2O with variable nitrogen loading, field work was carried out in four contrasted surface waters, e.g. waters in lakes (L01–L10), estuaries (E01–E03), urban rivers (R25–R35) and rural rivers (R01–R22) (as showed in Fig. 1 with L, E, and R in the beginning of series number). Besides that sampling sites of R23 and R24 were investigating for Haihe River, which located between urban and rural areas, were not taken into account for whole study. During sampling, all the river, lake and estuaries samples were collected

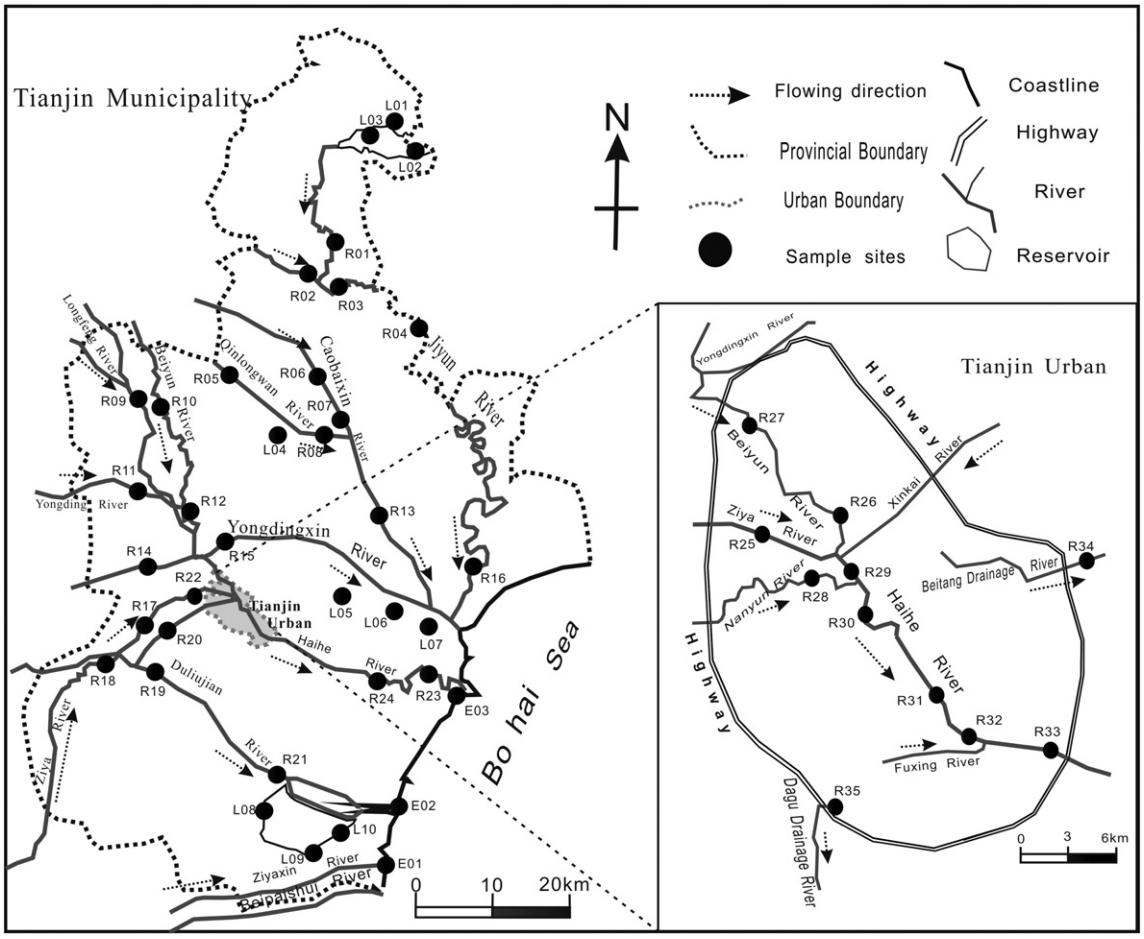

Fig. 1. Map of sampling site of surface waters in Tianjin river network.

Table 1
The environmental variables in different types of waters in Tianjin, China.

	Water temperature/°C	pH	TDS/mg·L^{-1}	DO/μmol·L^{-1}	DO saturation %
Estuaries	29.6 ± 1.2	8.1 ± 0.2	14440 ± 4780	212 ± 26	92 ± 10
Urban rivers	27.1 ± 1.2	7.8 ± 2.3	3529 ± 121	248 ± 88	105 ± 37
Rural rivers	28.1 ± 1.9	8.4 ± 0.9	1326 ± 1275	232 ± 110	98 ± 47
Lakes	30.1 ± 2.4	8.9 ± 0.4	2946 ± 6092	254 ± 45	111 ± 17

Data are average concentration ± mean deviation.

in the central part of water bodies to avoid the effects of the riparian zone.

For each sampling site, surface water samples (depth of 0.5 m) were collected using a 10-L Niskin sampler, then introduced into the bottom of a 50 mL serum bottle through a silicone tube. During bottle filling, at least two times volumes were allowed to overflow, and then amended with 10 mol·L^{-1} NaOH to increase the pH > 10, after which the bottles were sealed with rubber stoppers. The sample bottles were screw-capped with no head space and preserved in a cool place until analysis. For each sampling site, three samples in duplicate were collected and analyzed for dissolved N_2O within one week after the sampling.

2.3. Environmental variables

The water temperature (T), pH, dissolved oxygen (DO) and total dissolved solid (TDS) were measured in situ using an automated multi-parameter monitoring instrument (United States Gimcheon Instruments Inc. YSI 6600 v2). After collection, water samples were filtered through 0.22 μm membrane filters (Millipore) and cold stored in the dark until the concentrations of TN, NO_3-N, NH_4-N were measured using an automatic flow analyzer (SKALAR Sans Plus Systems).

2.4. N_2O measurement and flux calculation

For N_2O concentration measurements, the headspace equilibrium technique was used to determine the concentrations of dissolved gases. Specifically, approximately 20 mL of ultra-pure N_2 was injected into the sample bottle to displace the water. The bottles were then vigorously shaken for 30 min in a water bath at 25 °C to equilibration. The N_2O concentrations in the headspace were subsequently analyzed using an ECD-GC (HP6890) equipped with a packed Porapak Q (80/100 mesh) column (4.5 m × 3 mm). The column and ECD detector were conditioned at 50 °C and 320 °C, respectively. A mixture of Ar/CH_4 (95/5 v/v) was applied as the carrier gas at a flow rate of 20 mL min^{-1}. The formula described by Butler and Elkins (Butler and Elkins, 1991) was used to calculate the headspace gas concentrations, which were determined with a mean error of ±4%. The gas concentrations were expressed based on the degree of saturation relative to air:

$$\text{Degree of } N_2O_{saturation} = C_{N2O}/C_{N2Oatm} \times 100$$

$$C_{N2Oatm} = K \times C_A$$

where C_{N2O} is the measured concentration, C_{N2Oatm} is the concentration in equilibrium with the atmosphere of N_2O in water at the given water temperature, and C_A was the atmospheric N_2O concentration of the sampling sites. The C_{N2Oatm} in water was calculated by Henry's Law with K a temperature dependent constant.

The AOU (apparent oxygen utilization) and ΔN_2O were calculated as follows:

$$AOU = DO_{sat} - DO_{meas}$$

$$\Delta N_2O = C_{N2O} - C_{N2Oatm}$$

where DO_{sat} is the saturated dissolved oxygen (DO) concentration in water and DO_{meas} is the measured concentration of DO.

The exchange flux of N_2O at gas–water boundary layer of the surface water is calculated using:

$$F = K\Delta C = \frac{D}{Z}(C_s - C_{eq})$$

where F is the gas exchange flux, and ΔC is the difference between N_2O concentration in the air and water. K is the gas transfer velocity, and D is the gas diffusion coefficient that took the values of 1.08×10^{-5} cm^2/s (5 °C), 1.49×10^{-5} cm^2/s (15 °C), 1.98×10^{-5} cm^2/s (25 °C), and 2.53×10^{-5} cm^2/s (35 °C) in different temperatures (Lehrman, 1979). Z is the thickness of the boundary layer, which is an empirical constant that is related to wind speed (Emerson, 1975).

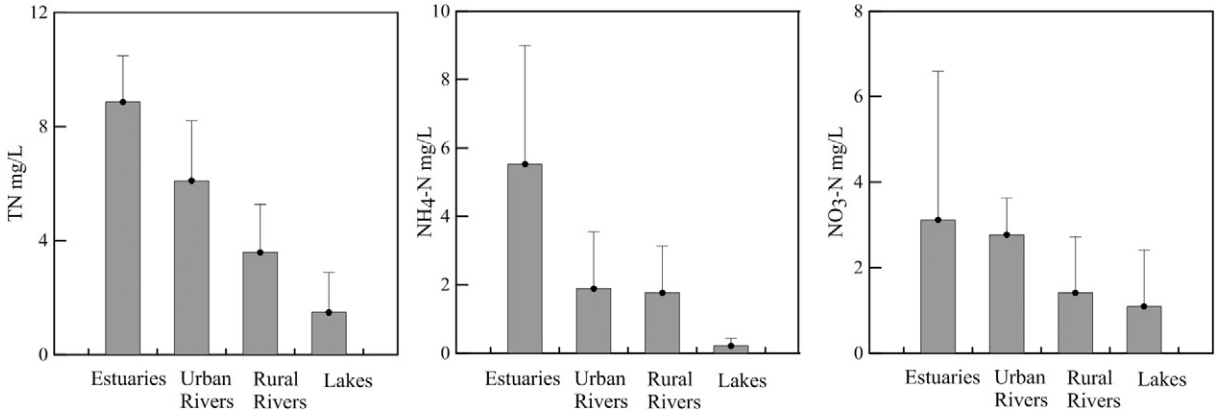

Fig. 2. Nitrogen species concentration in estuaries, urban rivers, rural rivers, and lakes in Tianjin.

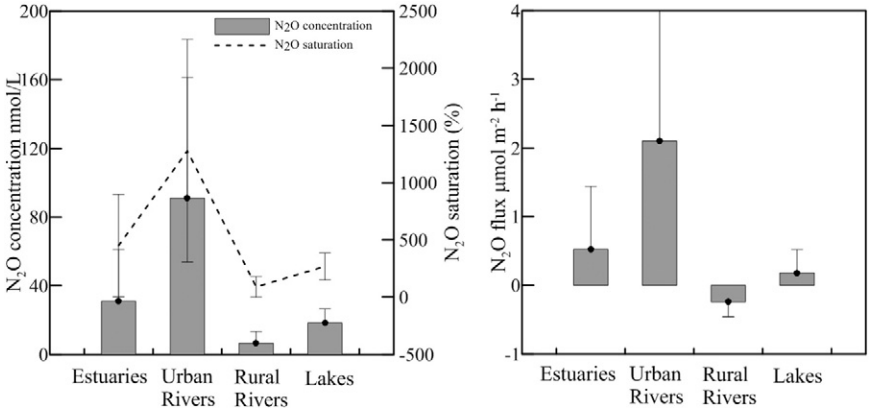

Fig. 3. N_2O concentrations, saturation, and fluxes in Tianjin river network.

2.5. Statistical analysis

Statistical analysis was done with Grapher 10.0 and Microsoft Excel for Windows 7. For all the analyses, the relationships between different parameters were considered statistically significant when $p < 0.05$.

3. Results

3.1. Environmental variables and nitrogen loading

The range and mean values of the main water parameters in this study including water temperature (T), dissolved oxygen (DO), total dissolved solid (TDS) and pH are listed in Table 1. Water temperature (T) displayed consistent variation among all the waters, while dissolved oxygen (DO), TDS and pH have considerable variability. DO in urban rivers and lakes was oversaturated, and the mean values of saturation were 105% and 110%, respectively. The DO saturation not only indicated that urban rivers and lakes were characterized by oxic conditions, but also provided information about eutrophic aquatic environment. However, DO in rural rivers and estuaries was under-saturated. The Tianjin river network was more saturated with respect to DO than the Shanghai river network, mostly under-saturated (with DO concentrations ranging from 2.84 to 6.14 mg/) (Yu et al., 2013) and displayed similar DO saturation with the San Joaquin River (45%–110% DO saturation) (Hinshaw and Dahlgren, 2013). Surface waters in estuaries were characterized by the highest salinity values (TDS ranging from 11.2 to 22.9 g/L), moderate pH values and the lowest DO level, typical of coastal saline water. TDS values in rural rivers were much lower than those in the urban ones, suggesting the influence of municipal point source discharges on urban rivers. Means and variances of pH in rural rivers (mean = 8.43) were obviously higher than those in urban rivers (mean = 7.80).

As shown in Fig. 2, spatial variations of nitrogen loading in Tianjin river network were observed within all of the sites during the study. District-averaged TN, NO_3-N, and NH_4-N contents were compared among four different types of surface waters as showed in Fig. 2 and a significant spatial variation was observed ($p < 0.05$). Estuary waters had the highest nitrogen loading among all, while urban rivers had obviously higher nitrogen loading than rural rivers and lakes seem to have lowest nitrogen loading ($p < 0.05$). When comparing NO_3-N, and NH_4-N contents among each type of surface water, the consistent of nitrogen loading will be indicated. For lakes and urban rivers, was primary DIN of the TN, while in rural rivers and estuaries, NH_4^+ content was higher than NO_3^-, indicating different N loads and source for different surface waters.

All the urban waters and estuaries and 70% (16 of 22 sites) of rural waters cannot meet V-class surface water quality according to Environmental Quality Standard for Surface Water (GB 3838-2002) (TN > 2 mg/L). When compared with N loading in Shanghai river network, urban rivers in Tianjin have lower NO_3^- (3.64–4.28 mg/L in Shanghai rivers) and NH_4^+ concentrations (3.04–5.76 mg/L in Shanghai rivers), while rural rivers have more N loads than Shanghai's (Yu et al., 2013). In addition, Tianjin river network had higher N loads than Guadalete River in Spain (Burgos et al., 2014). As reported in 2010 (Yue et al., 2010), nitrogen sources of Tianjin river network mainly were sewage for urban rivers, agricultural N input and industrial input for rural rivers, and multi-anthropogenic N inputs for estuaries. Actually, Tianjin river network is subjected to very complex N sources, some of which were effected temporally and spatially by many anthropogenic activities (i.e. sewage-dominated waters, discharges, and industrial

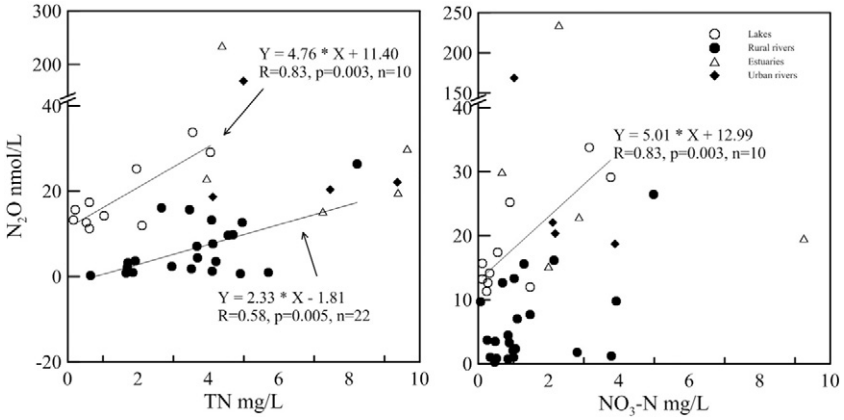

Fig. 4. Correlation between TN, NO_3-N and N_2O concentrations.

Table 2
Correlation between N_2O saturation and environmental variables in lakes.

	T	pH	EC	TDS	DO	TN	NH_4-N	NO_3-N	C-N_2O
T	1	0.046	0.214	0.214	−0.423	−0.259	0.14	−0.297	−0.05
pH		1	0.092	0.092	−0.086	−0.358	−0.083	−0.395	−0.597
EC			1	1.000**	−0.357	0.041	.746*	−0.131	0.232
TDS				1	−0.357	0.04	.745*	−0.132	0.231
DO					1	.699*	−0.332	.807**	0.592
TN						1	0.256	.974**	.829**
NH_4-N							1	0.044	0.256
NO_3-N								1	.829**
C-N_2O									1

"C-N_2O" means dissolved concentration of N_2O in water.
* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

wastewaters). The contrasts in concentrations of TN, NO_3^- and NH_4^+ indicated that the different surface waters had dramatically different N loading and N sources. Even though sample site covered a large scale of Tianjin municipal, N sources of all rivers differed a lot.

3.2. N_2O emission and saturation in different surface waters

Significant differences in the N_2O concentration and saturation were observed between different waters in Tianjin city (Fig. 2).

Specifically, high N_2O concentrations ranging from 18.71 to 234.33 nmol·L^{-1}were measured in urban rivers, with a mean value of 91.01 nmol·L^{-1}, corresponding to saturations of 252% to 3116%, respectively (Fig. 2). Conversely, in the rural rivers, the concentrations varied from 0.25 to 26.43 nmol·L^{-1}, corresponding to saturations of 3% and 354%, respectively. There appeared to be a significant spatial pattern in the N_2O concentrations and saturation of the surface waters in Tianjin. Urban rivers and lakes and estuaries in Tianjin were supersaturated with respect to atmospheric N_2O concentration (319 ppbv; IPCC, 2007), and thus were a source of N_2O to the atmosphere, while dissolved N_2O concentrations in rural rivers in Tianjin were mostly unsaturated (14 of 22 samplings). By comparison, the N_2O saturation and concentration values observed in rivers in Tianjin were slightly lower than those observed in rivers of Shanghai (rural rivers, mean saturation value: 300–450%; urban rivers, mean saturation value: 2500%) (Yu et al., 2013), and similar to that of San Joaquin rivers in California (values ranging from 118 to 429%) (Hinshaw and Dahlgren, 2013), and higher than Hudson rivers in New York (mean saturation value 185 ± 43%) (Cole and Caraco, 2001). For the lakes in Tianjin, mean N_2O averaged 18.44 ± 7.99 nmol·L^{-1}, corresponding to a saturation of 267 ± 117%, higher than that of lakes in NW Ontario, Canada, in which the N_2O concentrations were about 7.3 nmol·L^{-1} (0.44 μg·L^{-1}) (Hendzel et al., 2005), but obviously lower than that in eutrophic lakes and reservoirs (Harrison et al., 2005; Liu et al., 2011a; Wang et al., 2009).

3.3. Variation of calculated N_2O fluxes

Based on the climatological wind speed data provided by the meteorological observatory, conservative estimations for fluxes of N_2O in surface waters are calculated. N_2O fluxes showed similar variation with concentration and saturation in surface waters in Tianjin (Fig. 3), rural rivers represent a N_2O net sink with respect to atmosphere, with fluxes range of −0.51 to 0.35 μmol N_2O m^{-2} h^{-1}, averaged −0.24 μmol m^{-2} h^{-1}. In comparison, urban rivers have the highest N_2O fluxes among all surface waters, ranging from 0.11 to 5.23 μmol m^{-2} h^{-1} with an average of 2.10 μmol m^{-2} h^{-1}, lakes and estuaries in Tianjin are characterized by moderate N_2O fluxes ranging from −0.14 to 0.89 μmol m^{-2} h^{-1} (average 0.18 μmol m^{-2} h^{-1}) and from −0.26 to 2.08 μmol m^{-2} h^{-1} (averaged 0.52 μmol m^{-2} h^{-1}), respectively.

On the whole, N_2O flux variations at different surface waters in Tianjin were not simply related to nitrogen loading (Figs. 3 and 4). Both urban rivers and estuaries with the highest N loading emitted most N_2O among all the waters, however, rural rivers with high nitrogen loading characterized by N_2O fluxes were much lower than those of urban rivers and estuaries.

4. Discussion

4.1. N_2O production mechanisms

Water temperature, TDS, DO, pH and nitrogen loading were compared to N_2O concentration in Tianjin surface waters, and regression analysis was made between each of these variables with N_2O concentrations (Tables 2, 3, 4). Even though water temperature has been observed to affect N_2O production in some aquatic systems (Beaulieu et al., 2010), the lack of variability of temperature in this study prevents the observation of this relationship.

Table 3
Correlation between N_2O saturation and environmental variables in rural rivers.

	T	pH	EC	TDS	DO	TN	NH_4-N	NO_3-N	C-N_2O
T	1	0.131	0.279	0.003	0.239	−0.207	−0.261	−0.047	−0.222
pH		1	−0.072	−0.119	.856**	−0.082	−0.326	0.151	0.244
EC			1	.734**	−0.016	−0.275	−0.238	−0.157	−.425*
TDS				1	−0.122	0	0.09	−0.156	−0.416
DO					1	−0.115	−0.358	0.162	0.165
TN						1	.520*	.548**	.578**
NH_4-N							1	−0.317	0.188
NO_3-N								1	.480*
C-N_2O									1

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

Table 4
Correlation between N_2O saturation and environmental variables in urban rivers.

	T	pH	EC	TDS	DO	TN	NH_4-N	NO_3-N	C-N_2O
T	1	−0.5	.692*	.695*	−0.392	0.307	0.307	−0.284	0.237
pH		1	−0.228	−0.232	.966**	−0.17	−.722*	.673*	−0.38
EC			1	1.000**	−0.055	.643*	0.458	0.042	−0.374
TDS				1	−0.059	.643*	0.461	0.037	−0.375
DO					1	−0.149	−.701*	.689*	−0.466
TN						1	.678*	0.065	−0.254
NH_4-N							1	−0.569	−0.058
NO_3-N								1	−0.303
C-N_2O									1

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

The production of N_2O during nitrification and denitrification strongly depends on the pH, concentration of dissolved oxygen (DO) and N loading (e.g. Beaulieu et al., 2010; Rosamond et al., 2012). In our study, N_2O concentrations were positively correlated with DO ($R = 0.59$, $p = 0.008$), TN ($R = 0.83$, $p < 0.01$), and NO_3 ($R = 0.83$, $p < 0.01$) in lakes in Tianjin (Table 2), suggesting that increased DO and N loading promoted the production of N_2O, and also suggesting a significant nitrification source of N_2O (Garnier et al., 2006; Nevison et al., 2003). However, such correlations between N_2O concentrations and DO were not observed in other surface waters of Tianjin river network.

As an intermediate in denitrification (NO_3^- to N_2), N_2O may accumulate when O_2 is present and NO_3^- concentrations are high (Knowles, 1982). Effects of nitrogen loading on N_2O concentration were assessed by correlation analysis (Fig. 4). In rural rivers, N_2O production shows a significant correlation with TN ($R = 0.58$, $p < 0.01$), but no relationship with NO_3^- and NH_4^+ (Fig. 4 and Table 3). On one hand, the correlation shows that the increase of TN increasing under oxic conditions (DO > 100 μmol/L, see Table 1) will promote N_2O production in rural rivers, nitrification seems to be a primary process; on another hand, the fact that NH_4^+ in rural river was higher than NO_3^- (Fig. 2), associated with the observation that DO and most of N_2O in rural rivers stayed unsaturated through summertime, suggests that the denitrification of N_2O converted into N_2 dominated over nitrification in rural rivers (Beaulieu et al., 2011; Teixeira et al., 2010). We inferred that N_2O may be produced by coupled nitrification and denitrification at oxic/suboxic boundaries due to the transfer of intermediates such as nitrate and nitrite (Liikanen and Martikainen, 2003).

Consequently, obvious correlation between N_2O content and N loading was not observed in urban rivers, indicating the complexity of the influence of N loading on N_2O saturation and emissions. However, the positive relationship between DO and NO_3^- ($R = 0.69$, $p < 0.05$) and the negative relationship between DO and NH_4^+ ($R = -0.70$, $p < 0.05$) suggested that nitrification was the dominant process in urban waters. As noted previously for Tianjin river network, urban rivers are characterized by oxic condition with high DO saturation and associated with suitable temperature are a favorable environment for nitrification to produce N_2O (Garnier et al., 2006; Seitzinger et al., 2000); on the other hand, urban rivers in summertime often became eutrophic and that may result in anoxic condition at the interface of sediment–water, where denitrification could occur; however, algal blooms are common in eutrophied rivers during summer and may be another reason for high N_2O concentration (Weathers, 1984). In our former research (Yue et al., 2010), urban river waters were affected by different N sources (including urban sewage and discharge water from industry and agricultural activities) and uncertain distribution of point-source pollution, maybe this effect distinguishes the dominated process for N_2O production by comparing the nitrogen loading and N_2O concentration in urban rivers.

The relationship between N_2O saturation and other environment variables was not significant in estuaries. Even though estuaries had the highest N loadings, N_2O saturation was much less than that of urban rivers, suggesting that high salinity reduced the nitrification in estuaries (Rysgaard et al., 1999).

Fig. 5 shows the ΔN_2O plotted against the AOU for all samples. The good correlation observed for urban rivers, with a calculated slope of 0.34 nmol·L^{-1} ΔN_2O/μmol·L^{-1} AOU ($R = 0.78$, $p = 0.008$), suggested that nitrification was the key process for N_2O production. The regression coefficients for urban rivers in this study agree well with the reported coefficients for lakes and oceans (Cohen and Gordon, 1979; Mengis et al., 1997; Yoshinari, 1976). Relationship between ΔN_2O and AOU is often used to study the N_2O production processes in aquatic environment (Suntharalingam and Sarmiento, 2000), especially to evidence nitrification. No correlation was found for rural rivers, lakes, and estuaries.

4.2. Nitrogen loading and N_2O emission

According to our study, urban rivers displayed more saturated N_2O concentration and higher nitrogen loading than rural rivers and lakes, which was consistent with previous studies (Huttunen et al., 2003; Short et al., 2014; Stow et al., 2005). Rural rivers in Tianjin river network had high nitrogen loadings with low content of N_2O, which was consistent with some studies (Wang et al., 2009). To date, most of the studies concluded that N inputs and loadings have a positive but limited effect on N_2O saturation levels in the aquatic environment (Seitzinger et al., 2000; Short et al., 2014; Stow et al., 2005; Wang et al., 2009). While some studies suggested that variable N inputs and loadings act as the primary controls on the distribution of N_2O saturation levels and that the N_2O saturation level would increase significantly with increasing N inputs and loadings (Huttunen et al., 2003), some others did not (Outram and Hiscock, 2012).

Unlike natural rivers mainly influenced by agricultural or other natural N sources, observed N loadings in Tianjin surface waters are not readily explainable. Tianjin river network had been accumulating sewages, industrial wastewaters, and agricultural N input, from a large scale of Beijing and Hebei province (Yue et al., 2010). Urban rivers like Shanghai rivers and Tianjin river network are subject to more complex

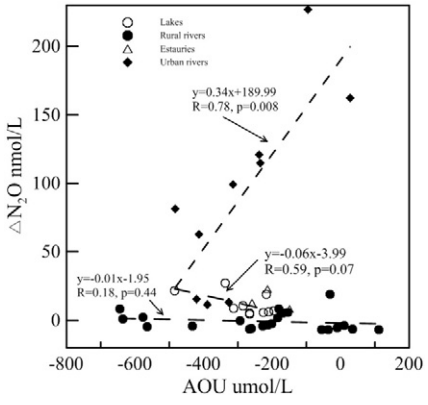

Fig. 5. ΔN2O versus AOU in surface waters in Tianjin region.

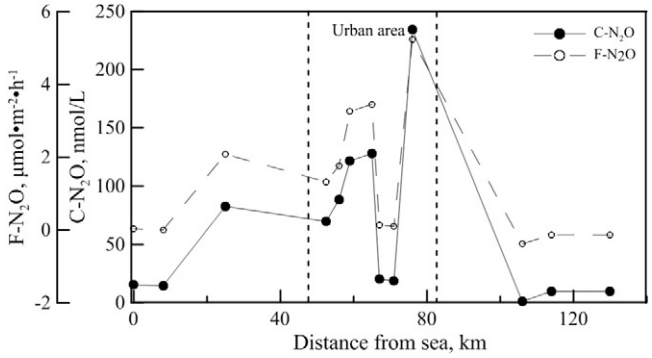

Fig. 6. N_2O variation along the river from inland rivers towards river mouth.

N sources, most of which are anthropogenic and spatiotemporally unpredictable (e.g. sewage-dominated N loadings, industrial wastewaters, and WWTP) (Yu et al., 2013; Yue et al., 2010), while rural rivers in Tianjin mainly received industrial wastewater and agricultural water. So we inferred that probably DO, DOC content, heavy metal pollution and the micros will essentially affect N_2O production. Our findings raise the possibility that NO_3^- concentrations indirectly affect N_2O emission and eutrophied rivers generally have more heavily saturated N_2O than other rivers worldwide (Beaulieu et al., 2008).

The IPCC method for estimating indirect N_2O emissions from aquatic systems received lots of dispute recently (Baulch et al., 2012; Hinshaw and Dahlgren, 2013; Yu et al., 2013). The proportion of leached N that is emitted as N_2O is termed an emission factor (EF), and for aquatic ecosystems, this is referred to as EF_5 (Baulch et al., 2012). Currently, EF_5 is set at 0.75% (kg N_2O-N per kg N leached), with an uncertainty range between 0.05% and 2.5% (IPCC, 2007). For Tianjin surface water, N_2O-N:NO_3-N ranged from 0.0028 to 0.058, averaging 0.020 in lakes; ranged from 0.0001 to 0.049, averaging 0.0042 in urban rivers; ranged from 0.0008 to 0.018, averaging 0.0008 in estuaries; and ranging from 0.0018 to 0.068, averaging 0.017 in urban rivers. The N_2O-N:NO_3-N in lakes and urban waters were significantly higher than IPCC setting value and higher than litter stream in San Joaquin rivers but lower than sediment–pore waters in San Joaquin rivers (Hinshaw and Dahlgren, 2013), suggesting that higher N loadings in urban rivers and lakes promote the N_2O emission significantly. The results also indicated that N_2O emission in urban rivers and lakes was probably underestimated than IPCC reported in 2007.

For urban rivers, denitrification and the addition of anthropogenic NO_3^- could lead to significant accumulations of N_2O (Cole and Caraco, 2001). In order to investigate N_2O accumulation in urban river in Tianjin river network, we chose a single river, Haihe River, for instance. From upstream to downstream, till to estuaries, we compare the N_2O spatial variation along the Haihe River (Fig. 6). Sampling sites on Haihe River, namely R09, R11, R12, R27, R26, R29, R30, R31, R32, R33, R24, R23, E03 are shown according to the distance to the sea in Fig. 6. In Tianjin urban rivers, there is an obvious tendency for N_2O concentrations and fluxes to be much higher in urban area than out of the urban area (Fig. 6), indicating that urban sewage and N loads actually result in N_2O accumulation in aquatic systems.

4.3. N_2O fluxes compared with other areas

Like many aquatic systems receiving high anthropogenic nutrient inputs, the environment in Tianjin river network, especially urban rivers and estuaries, is ideal for N_2O production and is likely to contribute significantly to N_2O emissions to the atmosphere. The N_2O fluxes of rivers and lakes around the world are listed in Table 5. Due to the heavy anthropogenic influence, extraordinarily high levels of N_2O were reported in some rivers such as South Platte and Neuse rivers (Garnier et al., 2006; McMahon and Dennehy, 1999; Stow et al., 2005) whereas some rivers and lakes were obvious sinks for N_2O (Hendzel et al., 2005). The estimated N_2O fluxes in rivers and lakes in Tianjin are comparable to fluxes in worldwide large rivers and lakes. Compared with other rivers and lakes, the calculated N_2O fluxes in the Tianjin river network were higher than those of most clean rivers but slightly less than those of contaminated rivers and eutrophied lakes. For example,

Table 5
Fluxes of N_2O in other related rivers, lakes and reservoirs.

	Names	Location	N_2O Fluxes ($\mu mol \cdot m^{-2} \cdot h^{-1}$)	References
Rivers	River Hudson	America	0.23 ± 0.14	Cole and Caraco (2001)
	River Swale–Ouse	England	14–100	García-Ruiz et al. (1999)
	River South Platte	America	0.27–97.02	McMahon and Dennehy (1999)
	River Neuse	America	~ −0.60 to 4.60	Stow et al. (2005)
	San Joaquin River	America	0.58–4.58	Hinshaw and Dahlgren (2013)
	Ohio river	America	0.24–0.38	Beaulieu et al. (2010)
	River Colne	England	0.04–0.17	Dong et al. (2004)
	River Millstone	America	0.25 (0.01–2.14)	Laursen and Seitzinger (2004)
	Spring-fed river	New Zealand	3.18 (1.86–5.00)	Clough et al. (2007)
	Toronto streams,	Canada	5.11 (4.87–5.34)	Baulch et al. (2012)
	Principal drainage streams	Mexico	21.46	Harrison et al. (2005)
	Xin'an Tang river	China	2.00 (1.47–3.13)	Xia et al. (2013)
	Shanghai river network	China	1.04–2.57	Yu et al. (2013)
	Tianjin river network	China	0.64 (−0.51 to 5.23)	This research
Lakes and reservoirs	Lake Taihu	China	−6.38 to 47.75 (Littoral Zone) −4.02 to 3.73 (Pelagic Zone)	Wang et al. (2006)
	Lake Taihu	China	0.41–0.58	Wang et al. (2009)
	Lake Mochou	Antarctica	0.22 ± 0.48	Liu et al. (2011b)
	Lake Tuanjie		0.18 ± 0.20	
	Lake Daming		0.51 ± 0.49	
	Three Gorges Reservoir	China	0.32 ± 0.48	Zhu et al. (2013)
	ELA in Ontario	Canada	<0.0033	Hendzel et al. (2005)
	Lake Kevaton	Finland	0.09–0.50	Huttunen et al. (2003)
	Hongjiadu (HJD)	China	0.45 (0.10–1.32)	Liu et al. (2011a)
	Wujiangdu (WJD)	China	0.64 (0.08–1.76)	
	Lake Nakaumi	Japan	1.07 (0.71–1.79)	Hirota et al. (2007)
	Lake Yuqiao and 6 other lakes	Tianjin, China	0.18 (−0.14 to 0.89)	This research

rivers in Tianjin had a greater N_2O flux than that of a hyper-eutrophic lake and an N-enriched river, i.e., Taihu Lake and Neuse River (Table 5). Additionally, the river network in Tianjin had much higher fluxes than a natural river, i.e., Colne River. Overall, even though the studied river had high N_2O fluxes, they were still moderate sources of N_2O emissions compared with soils and estuarine systems (Garnier et al., 2009; Seitzinger et al., 2000).

Based on the N_2O fluxes and the surface area of river network in Tianjin (about 884 km^2, including A channels and major tributaries from Haihe River, Yongdingxin River, Caobaixin River, and the Jiyun River) (data from Tianjin water resources bulletin in 2013), the annual emission from the rivers was estimated to be 2.07×10^5 mol N_2O (i.e., 5.78×10^3 kg $N\text{-}N_2O$) which was much lower than the N_2O fluxes from water bodies in the Seine Basin ($250–460 \times 10^3$ kg $N\text{-}N_2O$ yr^{-1}, Garnier et al., 2009) and South Platte and Potomac Rivers (2.5×10^5 kg N yr^{-1}; McMahon and Dennehy, 1999). Although the river network in Tianjin is not a significant source of N_2O due to the N_2O uptake by rural rivers, the huge number of rivers in China with similar characteristics could significantly contribute to N_2O emission and is of great concern (Yu et al., 2013).

5. Conclusion

N-enriched rivers were supposed to be an obvious N_2O emission source, while our findings did not raise the point exclusively. In Tianjin river network, urban rivers, lakes, and estuaries were supersaturated with respect to atmosphere, while rural rivers acted as N_2O sink, indicating that denitrification may continuously convert N_2O into N_2. The correlation between N_2O and DO and N loads indicated that N_2O production primarily occurred via nitrification in lakes and urban rivers. The production mechanisms were more complicated in rural rivers, and denitrification may be responsible for N_2O degradation. Sewage-dominated rivers mostly have higher N_2O emission and saturation than others, but few can be inferred for confirming the influence of pollutant on nitrification and denitrification. Compared to worldwide rivers and lakes, river network in Tianjin was globally a moderate source of N_2O but N_2O emissions from urban rivers and lakes indicated that globally aquatic N_2O emission rates and fluxes were probably underestimated in the 2007 IPCC report. In addition, rural rivers also absorbed atmospheric N_2O, acting as a N_2O sink. A better understanding of N sources in metropolitan rivers will improve N_2O emission assessment in future study.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.gexplo.2015.06.009.

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