



Nitrous Oxide Production in River Sediment of Highly Urbanized Area and the Effects of Water Quality

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Abstract Nitrous oxide (N₂O) is one of the main greenhouse gases, which contributes to the global warming and ozone destruction. Sediment cores and river water were collected from an urban and a suburban river for N₂O efflux measurement at the sediment-water interface and the factor-controlled incubations to investigating the N₂O effluxes under varying conditions of dissolved oxygen (DO), ammonium (NH₄⁺), nitrate (NO₃⁻) and sulfate (SO₄²⁻). Vertical profiles of dissolved N₂O concentrations in pore water were also acquired at eight depths. Results show that N₂O effluxes were higher at the urban site (13.01 ± 6.51 μg N m⁻² h⁻¹) than the suburban site (4.02 ± 2.01 μg N m⁻² h⁻¹). Oxygen consumption rates were optimal under high DO and NH₄⁺ amendment incubation, highlighting the strong nitrification potential in the sediment surface. Although N₂O effluxes at the urban site increased with the NO₃⁻ concentration under low DO condition, DO and NH₄⁺ concentrations in overlying water were the principal factors controlling N₂O effluxes (R = -0.415, *p* = 0.000 and R = 0.512, *p* < 0.05, respectively), indicating that nitrification greatly contributed to N₂O production, especially at suburban river. Generally, N₂O efflux was

substantially higher in the severely polluted urban river, and the sediments were the source of N₂O in river water.

Keywords Nitrous oxide · Production · River sediment · Factors · Urbanization area

Nitrous oxide (N₂O) is a potent greenhouse gas having a great impact on global climate change. Recent studies have pointed out that rivers with deteriorated water quality can be a significant source of atmospheric N₂O, and the role of rivers in global N₂O budgets is not well understood (Hinshaw and Dahlgren 2013; Yu et al. 2013). Nitrification and denitrification are currently considered as the most important microbial pathways of N₂O production in river systems (Beaulieu et al. 2011; Marty et al. 2011). Nitrification occurs in both the water column and surface sediments where oxygen is available, while denitrification, the dominant source of N₂O in rivers draining agricultural areas, predominately occurs in deeper anaerobic sediments (Meyer et al. 2008). In addition, coupled nitrification-denitrification, nitrifier denitrification and dissimilatory nitrate reduction to ammonium (DNRA) are also sources of riverine N₂O under specific conditions (Seitzinger and Kroeze 1998; Trimmer et al. 2006; Clough et al. 2007). Usually, coupled nitrification-denitrification occurs across the oxic/anoxic boundary in river sediments (Risgaard-Petersen 2003; Yan et al. 2012). Nitrifier denitrification, carried out by autotrophic nitrifiers, is favored under high ammonium (NH₄⁺), low oxygen and nitrate (NO₃⁻) concentrations, especially at the sediment surface (Wrage et al. 2001). DNRA requires reduced conditions with the presence of alternate electron donors, such as sulfide (Gardner et al. 2006).

As the substrates of nitrification and denitrification, dissolved NH₄⁺ and NO₃⁻ in the water column can freely diffuse into sediments and promote the generation of N₂O (Beaulieu

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et al. 2008). Dissolved oxygen (DO) is the key factor determining the relative importance of microbial N_2O production and consumption in river sediments. Pollutants in river water that affect the penetration of DO into river sediments may thus have impacts on N_2O effluxes at the sediment-water interface (Castro-González and Fariás 2004). Because NO_3^- is the primary form of nitrogen in rivers draining agricultural regions, N_2O emission factors were usually calculated as the ratio of leaching NO_3^- -N to N_2O -N (IPCC 2007). However, recent studies have indicated that the relationship between NO_3^- and N_2O production was not significant in urban rivers where high NH_4^+ concentrations promote more N_2O production from nitrification (Beaulieu et al. 2010; Rosamond et al. 2012). The sensitivity of nitrification and denitrification to environmental factors, e.g., DO, NO_3^- and NH_4^+ , may largely depend on anthropogenic nitrogen inputs in watersheds (Mulholland et al. 2008; Garnier et al. 2010). In addition, as an important component in geochemical cycling, sulfate (SO_4^{2-}) present in river water may favor a SO_4^{2-} -reducing condition in river sediments, which may directly or indirectly affect nitrification and denitrification rates due to the inhibitory effect of sulfide on nitrifier (Seitzinger 1988). However, the effects of these factors on the N_2O production at the river-sediment interface have rarely been quantified, especially the effects of NH_4^+ in urban rivers.

In our former study (Yu et al. 2013), by using the statistical analysis (simple linear regression analysis and stepwise multiple regression analysis) of the N_2O saturation with the environmental factors (DO, NH_4^+ , NO_3^- , etc.) from spatial and temporal measurement of 87 sites and 13 sampling campaigns, we found that NH_4^+ and DO level had great control on N_2O production and were better predictors of N_2O emission in urban watershed, and deduced that nitrification should also be the valid process of N_2O . Is it true? Or the statistical analysis was just a correlation between the data. In this study, a factor-controlled laboratory incubation was conducted to investigate N_2O effluxes at the river sediment-water interface and the effects of DO, NH_4^+ , NO_3^- and SO_4^{2-} in overlying water on N_2O production. The N_2O production mechanism will be discussed based the factor-controlled incubation data.

In this study, intact sediment cores were collected from urban river sites (Suzhou river) and suburban river site (Dianpu river), in the Shanghai urban and suburban area respectively. Factor-controlled laboratory incubations were conducted to investigate N_2O effluxes at the river sediment-water interface and the effects of DO, NH_4^+ , NO_3^- and SO_4^{2-} in overlying water on N_2O production. Dissolved N_2O concentrations in pore water were also measured at eight depths within the sediments. Based on these measurements, the production mechanisms of N_2O in sediments are discussed.

Materials and Methods

Study Area

Shanghai lies in the Yangtze River Delta and has a dense extensive river network. Total water area of the river network is 569.6 km², about 9 % of the Shanghai terrain (Yu et al. 2013). As a result of economic development and urban expansion, Shanghai river networks are seriously polluted by urban sewage release, especially in the highly urbanized central area. We set the sampling sites at two main rivers in the urban and suburban area of Shanghai, respectively. Urban river site (Suzhou river) was heavily polluted by NH_4^+ and organic pollutants during urban development, while suburban river (Dianpu river), located in upstream Huangpu river, has relatively better water quality. The large differences in the physiochemical properties of river water and sediments between these two sampling sites provides basis for studying the spatial variance of riverine N_2O flux at sediment-water interface and the mechanisms of N_2O production.

Samples Collection and Measurement

At each site, 140 intact sediment cores (from 6 to 10 cm long), overlying water and ambient air were collected and transported to the laboratory. Sediment cores were collected by a sediment corer, which contains a sampling tube (volume: 218 ml; dimension: 24 cm long and 3.4 cm internal diameter) made of plexiglass with two butyl-rubber septum and screwed caps on the bottom and top. Twenty liters of surface water was collected by a plastic bucket for in-situ condition incubation. Three water samples were also collected at each site using the same sampling tubes for in-situ dissolved N_2O concentration determination. Three in-situ air samples were taken and stored in air bags for ambient N_2O concentration determination. Additional water sample (500 ml) were collected to measure water quality parameters. All water samples were stored in a cooler with ice (0–4 °C) and transported back to the lab. During the samplings, portable sensors were used to measure in-situ water temperature and DO concentration (M-2, Myratek, USA), salinity (YSI-30, YSI, USA), and pH (HQ40d-IntelliCAL, HACH, USA.).

In the laboratory, 0.2 mL HgCl_2 solution was injected into the water sampling tubes to inhibit bacterial activity (Butler and Elkins 1991), and the tubes were then stored under 0–4 °C for dissolved N_2O measurements. Water samples for river chemistry were filtered with 0.45 μm filter and then stored in polyethylene bottles at –20 °C. Top 4 cm of three sediment cores from each site was sliced into 0.5 cm layer subsamples. Subsamples were freeze dried and bulk density and moisture content of each subsample were determined from the weight loss. After grinding and sieving (250 μm), dried subsamples were stored in ziploc bags until further analysis.

Dissolved NO_3^- , NO_2^- , SO_4^{2-} and sediment extractable NO_3^- (extracted by $1 \text{ mol}\cdot\text{L}^{-1}\text{KCl}$) (Buljan 1951) were analyzed by a continuous flow analyzer (FUTURA, Alliance, French). Spectrophotometry was used for the measurement of dissolved NH_4^+ concentration in river water (Krug et al. 1979) and extractable NH_4^+ of sediments (extracted by $1 \text{ mol}\cdot\text{L}^{-1}\text{KCl}$) (Buljan 1951). Dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) concentrations were analyzed by a TOC analyzer (vario TOC, Elementar, Germany) with high temperature digestion and catalytic post combustion, and TN and TS content of sediments were analyzed by an elemental analyzer (vario MICRO cube, Elementar, Germany) with combustion method. Potassium dichromate volumetric method was used to determine the content of organic carbon of sediments (SOC) (Yeomans and Bremner 1988). Laser particle size analyzer (LS 13320, Beckman Coulter, USA) was used to measure the sediment grain size distribution.

Incubation and N_2O Measurement

Before the incubation, sediment cores were adjusted to 4 cm length. Besides the in-situ condition incubation (in-situ river water used), sediment cores were divided into two DO controlled groups, high DO and low DO. In each DO controlled group, dissolved NH_4^+ , NO_3^- , $\text{NH}_4^++\text{NO}_3^-$ and SO_4^{2-} concentrations of overlying water were adjusted to achieve five concentration gradients. Ammonium chloride (NH_4Cl), potassium nitrate (KNO_3) and sodium sulfate (Na_2SO_4), and deionized water were used to formulate the solutions for factor-controlled incubation (Table 1). To ensure the availability of organic carbon in the incubation, sodium acetate (NaAC) was used to adjust DOC concentration to 50 mg/L in the formulated solution. Ambient air and compressed high purity nitrogen gas were pumped into the formulated solution to form high and low DO concentration conditions, respectively. Six cores were used for each factor and DO controlled incubation, in which three of them were for the measurement of DO

consumption by the sediments and the rest for N_2O efflux measurement. All incubations were conducted at 20°C .

The concentrations of N_2O and DO in the overlying water were measured before and after incubation (4 h). Pore water N_2O concentration in sediments under in-situ condition incubation and factor-controlled incubation with the maximum concentration amendment were then measured. DO was measured directly by a DO meter (LDO101, HACH, USA). Static headspace equilibrium technique was used for the measurement of dissolved N_2O concentration in in-situ water samples, incubation water samples and sediment pore water (Yu et al. 2013). Briefly, for the in-situ surface river water samples, 60 mL ultrahigh purity nitrogen gas was injected into a tube by a plastic syringe through the top septum of the tube, while a needle penetrating into the bottom septum allowed an equal volume of water to escape. The sampling tube was then shaken vigorously for 5 min to equilibrate N_2O between the headspace and water phase. For the sediment-water incubations, 60 ml overlying water in incubation tube was transferred into another empty tube (with ambient air) by a plastic syringe, and the tube was then quickly capped. After vigorous shaking, headspace air was analyzed for N_2O . For the sediment pore water measurement, sediment cores were sliced into 0.5 cm intervals. Each slice of sediment was quickly put into a tube containing 60 mL deionized water. The tube was quickly capped and vigorously shaken to form a slurry in the tube, and headspace N_2O concentration was measured. At the same time three tubes containing 60 mL deionized water were also measured as the background. Ten ml headspace sample of the tube was drawn out and injected into a gas chromatograph (GC) (HP7890A, Agilent, USA) for N_2O analysis, which was equipped a 1-ml sample loop. And a 95 : 5 mixture of Ar/CH_4 was used as the carrier gas. The detection limit was about 20 ppbv (about $1 \text{ nmol N}_2\text{O l}^{-1}$). And the measurement precision was less than 1 % relative standard deviation (six consecutive measurements) at approximately ambient concentrations (347.7 ppbv N_2O standard). After N_2O measurement, the slurry in tubes was filtered with $0.45 \mu\text{m}$ filter and stored in -20°C waiting for pore water chemistry analyses. N_2O

Table 1 The concentration gradient of factors in controlled incubation

Control factor	Method	Concentration grade										
		High DO control group					Low DO control group					
DO (mg/L)	Aerating air or N_2	9.33 ~ 9.60					1.20 ~ 1.53					
NH_4^+ (mg N/L)	NH_4Cl added	0	5	10	20	25	0	5	10	20	25	
NO_3^- (mg N/L)	KNO_3 added	0	5	10	20	30	0	5	10	20	30	
$\text{NH}_4^++\text{NO}_3^-$ (mg N/L)	NH_4Cl and KNO_3 added	0 + 0	5 + 5	10 + 10	20 + 20	25 + 30	0 + 0	5 + 5	10 + 10	20 + 20	25 + 30	
SO_4^{2-} (mg/L)	Na_2SO_4 added	0	30	60	120	300	0	30	60	120	300	
DOC (mg/L)	NaAC added	50	50	50	50	50	50	50	50	50	50	

concentrations in laboratory ambient air and in ultrahigh purity nitrogen gas (in case of any contamination) used in the incubations were also measured.

Calculation

Fluxes of DO and N₂O at sediment-water interface were calculated according to the concentration changes in overlying water at the end of incubations as against the initial conditions at the beginning:

$$F = (C_{W-E} - C_{W-B})V/S/T \quad (1)$$

Where F is the flux of DO ($\text{mg m}^{-2} \text{h}^{-1}$) or N₂O ($\mu\text{g N m}^{-2} \text{h}^{-1}$) at the sediment-water interface; V is the volume of overlying water (L); C_{W-E} and C_{W-B} are the DO (mg/L) or N₂O ($\mu\text{g N/L}$) concentration in overlying water at the end and beginning of incubation; T is the incubation time (h) and S is the cross-sectional area of sediment core (m^2).

DO concentration was measured directly. N₂O concentration in water (C_W) is calculated based on the concentrations of N₂O in the headspace of tube:

$$C_W = ((C_{H-m} - C_{A-m})V_H + \alpha C_{H-v}V_W)/V_W \quad (2)$$

where C_{H-m} and C_{H-v} are the mass concentration ($\mu\text{g N/L}$) and volume concentration (ppbv) of N₂O in the headspace of tube under equilibrium state; C_{A-m} is the mass concentration of N₂O in the lab air or ultrahigh purity nitrogen gas injected into the tube ($\mu\text{g N/L}$); V_H is the volume of tube headspace (L); α is the solubility coefficient of N₂O in water (Weiss and Price 1980); V_W is the volume of water in the tube (L).

The concentration of N₂O in sediment pore water (C_P) is calculated according to dissolved N₂O concentration in the slurry and deionized waters:

$$C_P = (C_S(V_P + V_{DIW}) - C_{DIW}V_{DIW})/V_P \quad (3)$$

Where C_S and C_{DIW} are the mass concentrations of N₂O in slurry and deionized water in tube, respectively ($\mu\text{g N/L}$); V_P is the pore water volume in 0.5 cm sediment layer (L); V_{DIW} is the volume of deionized water in tube (L); C_B , C_S , and C_{DIW} are computed based on the equation (2).

Saturation of N₂O in river water is calculated according to the in-situ dissolved N₂O concentration in river water (C_W), and the calculated saturated N₂O concentration corresponding to ambient air N₂O concentration:

$$S_{N_2O} = C_W/C_{S-Ambient} = C_W/(\alpha C_{Ambient})100\% \quad (4)$$

Where C_W is from the equation (2), $C_{Ambient}$ is the volume N₂O concentration of in situ ambient air (ppbv); α is the solubility coefficient of N₂O in water (Weiss and Price 1980).

Results

Urban and Suburban River Water and Sediment Characteristics

In this study, river water from the urban site had lower DO concentration and higher NH₄⁺ and NO₃⁻ concentrations than the suburban site, while suburban site sediment pore water had higher NO₃⁻ concentrations than sediment at the urban site (Table 2). Except for extractable NO₂⁻ and medium particle size, all the other parameters of river sediments were higher at the urban site than at the suburban site, especially the sediment organic carbon (SOC) and extractable NH₄⁺ (Table 2). The suburban river (Dianpu river) located in the upstream of Shanghai river network had better water quality than urban river (Suzhou river).

N₂O Concentration and Saturation in River Surface Water

In situ dissolved N₂O concentrations of surface river water at suburban and urban sites were $0.51 \pm 0.13 \mu\text{g N/L}$ and $2.68 \pm 0.41 \mu\text{g N/L}$, respectively. Corresponding to the ambient N₂O concentration in atmosphere, the saturations of N₂O were $330 \pm 84.0 \%$ and $2625 \pm 401.6 \%$ at the suburban and urban sites, respectively.

Vertical Variation of Sediment Properties

Urban river sediments had higher moisture content than suburban river sediments, while the suburban river sediments had larger medium particle size (Fig. 1). Except for extractable NO₂⁻ which was higher in the suburban river sediments, other parameters of the urban river sediments were greater than those of suburban river sediments, while the extractable NO₃⁻ were comparable in both sites. SOC decreased slightly from surface to bottom sediments at both sites. Extractable NH₄⁺ of sediment was constant over the depth at the suburban site while it fluctuated at the urban site. Extractable NO₃⁻ of sediments at both sites increased identically within 1 cm and then decreased in deeper sediment, while extractable NO₂⁻ and total sulphur (TS) exhibited an increasing trend from surface to bottom at both sites. Extractable NH₄⁺ was the main nitrogen form among the sediment extractable nitrogen.

Sediment pore water profiles within 0–4 cm depth are shown in Fig. 2. Vertical profiles of DOC and NH₄⁺ concentrations in pore water were similar at the suburban and urban site, but were significantly higher at the urban site ($p = 0.000$). However, the concentrations of NO₃⁻ and SO₄²⁻ in pore water were higher at the suburban site, which also decreased from the surface to the deeper layer. As seen with extractable nitrogen in the sediments, NH₄⁺ was the main form of dissolved nitrogen in pore water.

Table 2 Parameters of surface water, average of parameters of pore water and properties of top 4 cm at suburban site and urban site (SS: suburban site; US: urban site.)

	Site	Salinity (ppt)	pH	DO (mg/L)	DIC (mg/L)	NH ₄ ⁺ (mg N/L)	NO ₃ ⁻ (mg N/L)	NO ₂ ⁻ (mg N/L)	DOC (mg/L)	SO ₄ ²⁻ (mg/L)
Surface water	SS	0.4	7.3	8.06	27.1	1.14	3.48	–	24.2	135
	US	0.4	7.6	2.84	31.2	3.88	6.64	–	26.4	123
Pore water	SS	–	–	–	–	23.9	2.94	3.1	165	994
	US	–	–	–	–	86.4	1.14	1.97	852	735
	Site	–	Medium particle size (μm)	Moisture (w/w: %)	SOC (mg/g)	NH ₄ ⁺ (mg N/kg)	NO ₃ ⁻ (mg N/kg)	NO ₂ ⁻ (mg N/kg)	TN (mg N/g)	TS (mg S/g)
Sediment	SS	–	17.7	64.5	9.8	29.7	2.68	2.73	0.83	0.89
	US	–	13.8	85.9	15.5	45.6	3.11	2.3	1.32	1.38

DIC dissolved inorganic carbon, DOC dissolved organic carbon SOC, sediment organic carbon, TN, total nitrogen TS, total sulfur

DO Consumption Rates

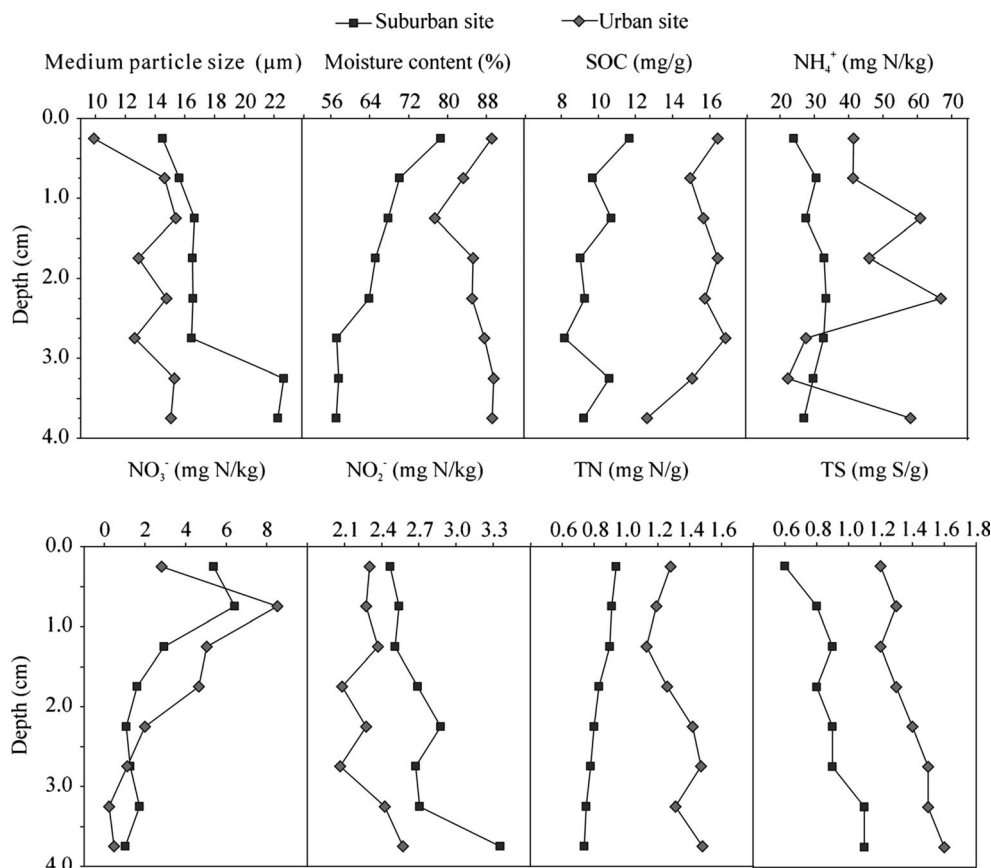
Consumption rates of DO were higher under high initial DO concentration (9.33–9.60 mg/L) than under low DO (1.20–1.53 mg/L), and higher at the urban site than at the suburban site, which indicated more rapid oxygen consumption microbial activities at the surface of urban sediments (Fig. 3). Furthermore, DO consumption rates increased with the concentration of NH₄⁺ or NH₄⁺+NO₃⁻ in the overlying water at both sites. In particular, the DO consumption rate at the urban site

reached 0.01 mg m⁻² h⁻¹ under high DO conditions when the NH₄⁺ concentration in the overlying water was 20 mg N/L. However, DO consumption did not show any correlation with NO₃⁻ and SO₄²⁻ concentration (Fig. 3).

N₂O Fluxes at the Sediment-Water Interface

N₂O fluxes at the sediment-water interface were higher at the urban site (13.01 ± 6.51 μg N m⁻² h⁻¹) than at the suburban site (4.02 ± 2.01 μg N m⁻² h⁻¹) under incubation conditions

Fig. 1 Vertical profiles of sediment properties at the suburban site and urban site



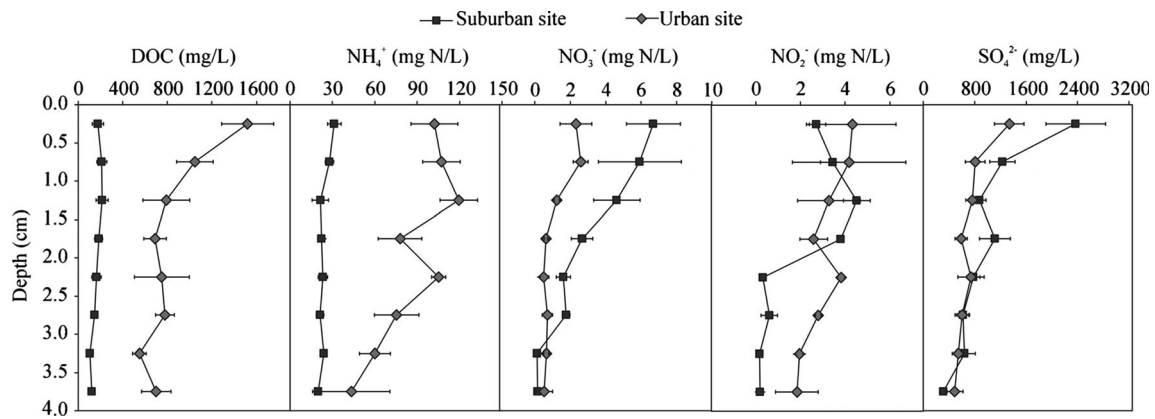


Fig. 2 Profiles of pore water at the suburban site and urban site (Error is the standard deviation of triple samples)

approximating site conditions. N_2O fluxes were also higher at the urban site than at the suburban site under almost all other factor-controlled incubations. DO significantly affected N_2O fluxes at the sediment-water interface at both sites ($p = 0.000$, paired t-test). Generally, higher N_2O fluxes were observed under low DO conditions. The amendment of NH_4^+ and $NH_4^+ + NO_3^-$ stimulated the N_2O fluxes at the sediment-water interface (Fig. 4). N_2O fluxes at the suburban site reached $42.8 \pm 18.5 \mu g N m^{-2} h^{-1}$ under low DO condition when NH_4^+ concentration was 25 mg N/L, which was 10.6 and 6.7 times higher than those in the in-situ condition incubation using in-situ river water ($4.02 \pm 2.01 \mu g N m^{-2} h^{-1}$, NH_4^+ : 1.14 mg N/L) and controlled incubation with no NH_4^+ added ($6.39 \pm 4.18 \mu g N m^{-2} h^{-1}$). N_2O flux at the urban site

reached a maximum of $81.2 \pm 42.2 \mu g N m^{-2} h^{-1}$ under low DO conditions when NH_4^+ concentration was 20 mg $N \cdot L^{-1}$. This was 6.2 and 7.6 times higher those in the incubation approximating site conditions ($13.0 \pm 6.51 \mu g N m^{-2} h^{-1}$, NH_4^+ : 3.88 mg N/L) and controlled incubation ($10.6 \pm 4.15 \mu g N m^{-2} h^{-1}$). The amendment of NH_4^+ and NO_3^- together had a stronger promoting effect on the emissions of N_2O at the sediment-water interface as well. Under low DO conditions, when $NH_4^+ + NO_3^-$ concentration was 10 + 10 mg N/L, N_2O flux at the suburban site was $72.1 \pm 29.3 \mu g N m^{-2} h^{-1}$. When the mixed concentration was 25 + 30 mg N/L, N_2O flux at the urban site reached $123.5 \pm 31.0 \mu g N m^{-2} h^{-1}$. However, adding NO_3^- individually into overlying water did not significantly stimulate the

Fig. 3 DO consumption rates under different factor controlled incubation

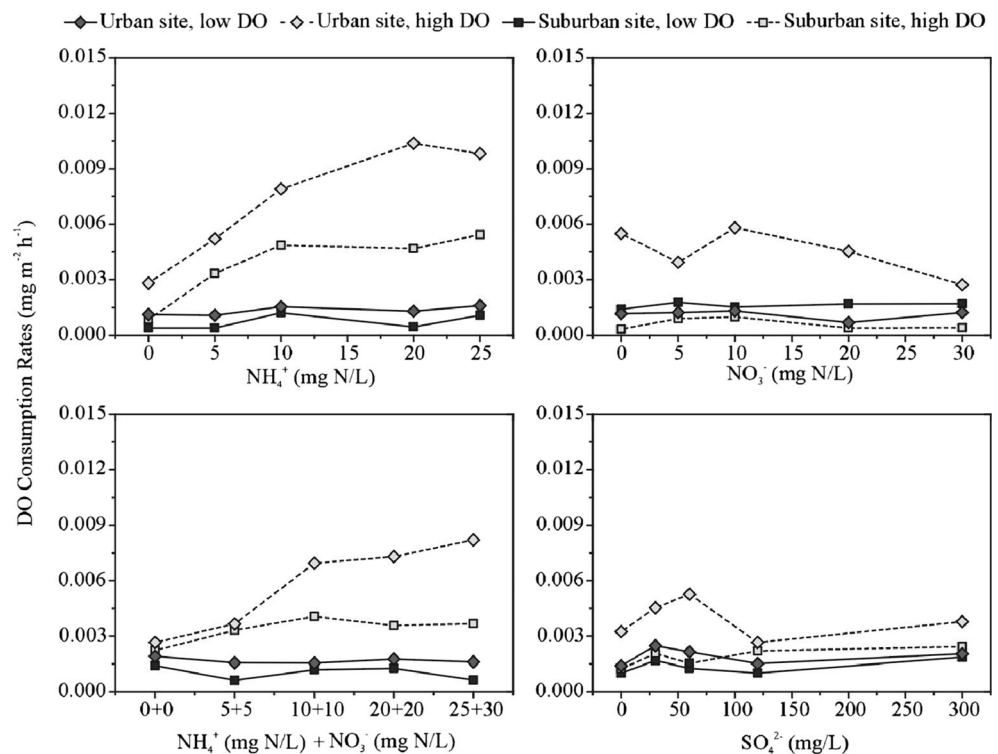
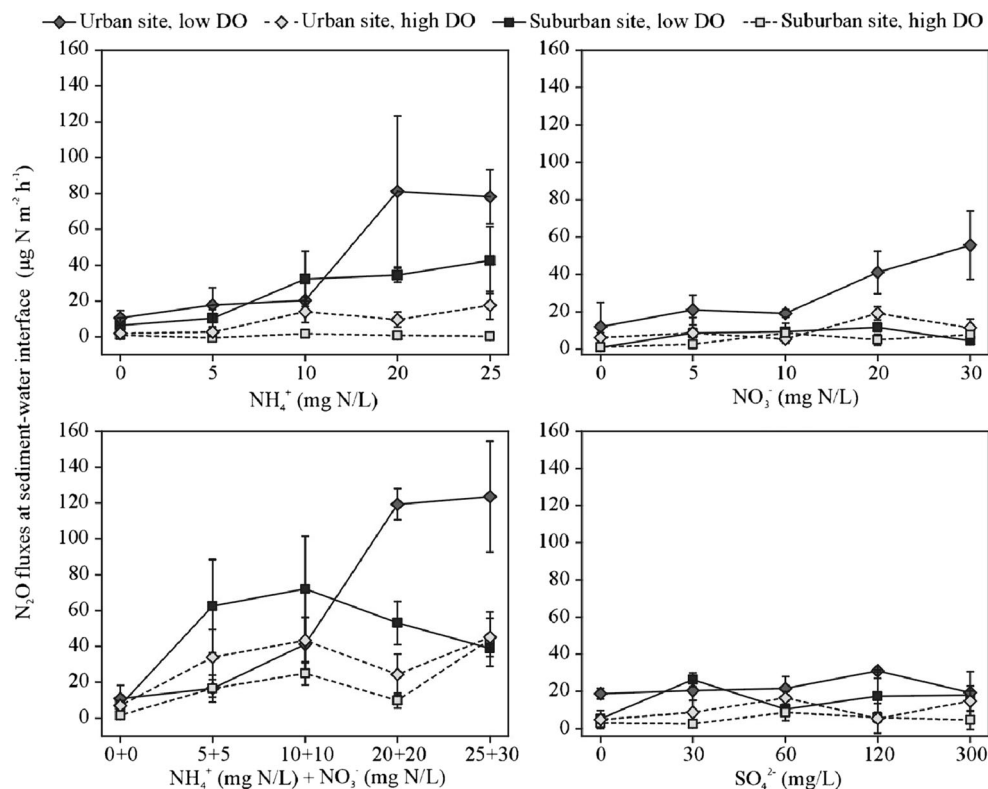


Fig. 4 Emission fluxes of N_2O at the sediment-water interface under different factor controlled incubation (Error is the standard deviation of triple samples)



N_2O fluxes at the sediment-water interface, except at the urban site under low DO conditions. There was no significant difference between N_2O fluxes under simultaneous NH_4^+ and NO_3^- amendment and the sum of the fluxes of NH_4^+ and NO_3^- when added separately ($p > 0.05$), indicating little collaborative effect of NH_4^+ and NO_3^- on microbial N_2O production in the sediments. Sulfate amendments in the overlying water had no influence on N_2O releases from the sediments ($p > 0.05$) (Fig. 4).

The Vertical Distribution of N_2O in Pore Water

In all observed profiles of pore water N_2O , the highest N_2O concentration appeared in surface sediment at 0–1 cm in both suburban and urban sites. Below 1 cm depth, N_2O concentrations decreased quickly to undetectable levels (Fig. 5). Pore water N_2O concentrations at the surface 0–1 cm layer at the suburban and urban sites were $1.52 \pm 1.04 \mu\text{g N/L}$ and $2.81 \pm 0.96 \mu\text{g N/L}$ respectively, which were higher than the N_2O concentration of in-situ surface river water ($0.51 \pm 0.13 \mu\text{g N/L}$ and $2.68 \pm 0.41 \mu\text{g N/L}$, respectively). There were significant differences in pore water N_2O between high and low DO conditions ($p < 0.01$). Low DO condition favored the production of N_2O at 0–1 cm pore water, and amendments of NH_4^+ and $NH_4^+ + NO_3^-$ had positive influences on N_2O as well. Under low DO conditions, $NH_4^+ + NO_3^-$ amendment increased the concentration of N_2O at 0–0.5 cm pore water to $6.13 \pm 5.40 \mu\text{g N/L}$ and to

$2.46 \pm 1.75 \mu\text{g N/L}$ at a depth of 1–1.5 cm. The NO_3^- or SO_4^{2-} amendments had no significant effects on N_2O concentrations in pore water ($p > 0.05$). Moreover, pore water N_2O concentrations were higher at the urban site than at the suburban site under all conditions (Fig. 5).

Discussion

Oxygen consumption rates at both suburban and urban sites were higher under high DO condition than those under low DO condition, indicating the high potential of aerobic metabolism in the surface sediments when DO was abundant. On the other hand, oxygen consumption rates at the urban site were higher than the suburban site under either high or low DO conditions (Fig. 3) due possibly to high concentrations of DOC and NH_4^+ , the substrates of aerobic respiration, in the pore water of urban river sediments and also the higher SOC (Table 1 and Fig. 2). Decomposition of organic carbon and nitrification consumed DO in the overlying water such that high organic carbon content and NH_4^+ in the sediments and pore water accelerated the consumption of DO (Jäger et al. 2011). When NH_4^+ and $NH_4^+ + NO_3^-$ were amended, the DO consumption rates at the urban and suburban site sediments markedly increased (Fig. 3), implying that the nitrifiers in the surface sediments converted NH_4^+ into NO_3^- while consuming DO (Conrad 1996; Megonigal et al. 2003). At the urban site, NH_4^+ concentrations in overlying water had a significant

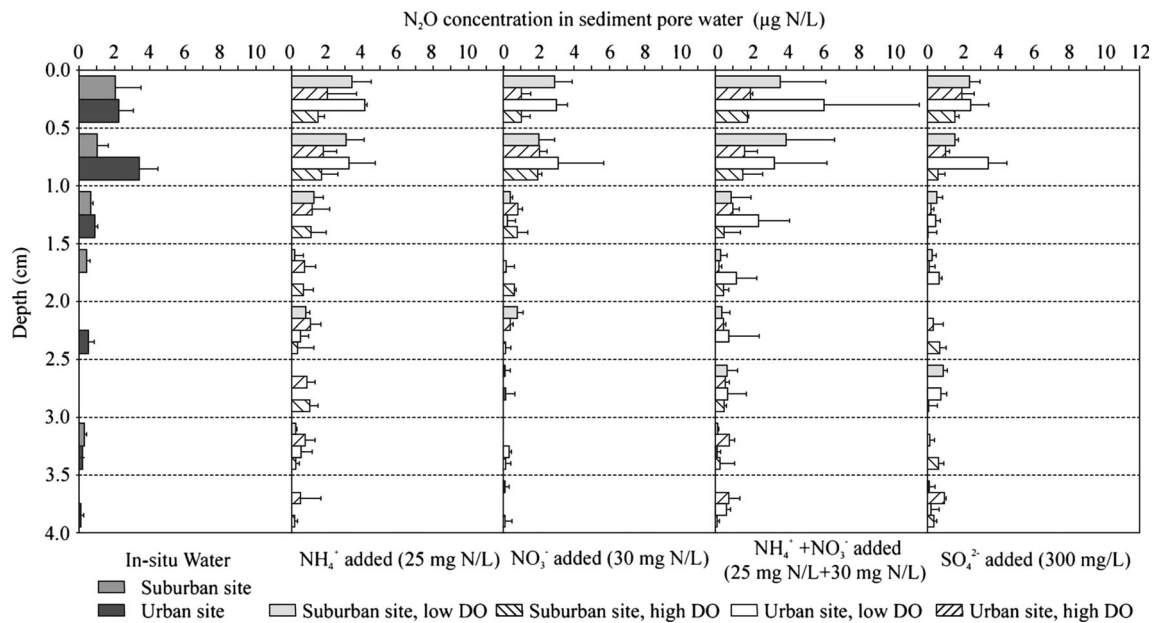


Fig. 5 Vertical Profiles of N₂O concentrations in sediment pore water in natural state and under the maximum factors concentration incubation (Error is the standard deviation of triple samples)

correlation to DO consumption rates ($R = 0.943$, $p < 0.05$) under high DO conditions. The diffusion of high concentrations of NH₄⁺ from overlying waters into surface sediments could stimulate the nitrification process and result in large amounts of oxygen being consumed by sediments in the urban site (Casciotti et al. 2010). The absence of a relationship between NH₄⁺ in overlying waters and DO consumption rates at the suburban site ($p > 0.1$), indicates a low potential of aerobic metabolism and abundance of heterotrophic microorganisms in the surface sediments.

In general, denitrification is considered to be a major source of N₂O because NO₃⁻ is found in various aquatic ecosystems as the dominant nitrogen species. However, in urban rivers which are polluted mainly by domestic wastewater, NH₄⁺ is present with comparable abundance as NO₃⁻ or even higher. The importance of denitrification should be given further consideration. Previous research reveals that nitrification can also be a main source of N₂O in riverine and estuarine areas strongly influenced by human activities (Barnard et al. 2005; Gribsholt et al. 2005) and with low DO and high NH₄⁺ environments (Yu et al. 2013). Liu et al. (2011) found that N₂O concentration in reservoirs was positively correlated with NH₄⁺ and NO₃⁻ and a linear correlation was found between N₂O production and apparent oxygen utilization, indicating that N₂O was mainly from nitrification, which was the dominate process response for the N₂O production in the reservoirs. IPCC assumed that N₂O produced by nitrification was two times higher than that from denitrification for lakes and rivers (IPCC 2007). Some studies have shown that NH₄⁺ concentration was positively correlated with N₂O saturation (Wang et al. 2009) and N₂O fluxes (Teixeira et al. 2010;

Morse et al. 2012). On the other hand, if N₂O was produced in denitrification it should take place in the deeper anaerobic sediment, and N₂O produced from nitrification in the aerobic upper layer of sediments could diffuse out and thus contribute more to N₂O efflux. Meyer et al. (2008) showed that, 82 % of N₂O produced in river sediment was consumed before diffusing into water when NO₃⁻ was added and 87 % of the N₂O emission into the atmosphere was from nitrification that occurred in the surface sediment.

Oxygen affects the strength of nitrification and denitrification, the NO₃⁻ generation rate, and the activity of N₂O reductase. For example, higher DO inhibited denitrification and N₂O production and yield in denitrification (Naqvi et al. 2000) and lower O₂ condition could enhance the yield of N₂O in nitrification (Goreau et al. 1980). The yield of N₂O per mole of NH₄⁺ oxidized increased from 0.25 % at high O₂ (~20 %) concentrations to nearly 10 % at low O₂ (0.5 %) concentrations (Seitzinger et al. 1983). In our study, N₂O fluxes at the sediment-water interface at both suburban and urban site were higher under low DO condition than high DO condition ($p < 0.0001$). Amendment of NH₄⁺ or NH₄⁺+NO₃⁻ significantly increased N₂O fluxes ($p < 0.05$, $p < 0.05$, respectively), but NO₃⁻ and SO₄²⁻ had no significant impact (Table 3). Moreover, significant differences in the vertical profiles of N₂O concentration were found between high DO and low DO treatments ($p < 0.01$) and NH₄⁺ and NH₄⁺+NO₃⁻ amendment increased N₂O concentrations in pore water of top 0.5 cm under low DO condition (Fig. 5). DO and NH₄⁺ in overlying water were the main factors controlling N₂O concentrations in pore water and the fluxes of N₂O at the sediment-water interface. Low DO concentration in overlying

Table 3 The correlation analysis between water quality parameters and oxygen consumption rates, and the fluxes of N₂O at sediment-water interface (* $p < 0.05$, two tailed; ** $p < 0.01$, two tailed)

		NH ₄ ⁺ (mg N/L)	NO ₃ ⁻ (mg N/L)	NH ₄ ⁺ +NO ₃ ⁻ (mg N/L)	SO ₄ ²⁻ (mg/L)	DO (mg/L)
N ₂ O fluxes (μg N m ⁻² h ⁻¹)	R	0.512*	0.41	0.537*	0.145	-0.415**
	<i>p</i>	0.021	0.073	0.015	0.543	0.000
	<i>n</i>	20	20	20	20	80

water promoted N₂O production in the sediments and had a greater effect than NO₃⁻ on controlling N₂O fluxes (Rosamond et al. 2012). Weak relationship between NO₃⁻ and N₂O fluxes indicates that denitrification may not be the primary process in these two sites. We can also exclude nitrifier denitrification and DNRA as the production mechanism of N₂O in these two river sites. The high DOC concentration of in-situ or factor-controlled incubation cores did not favor nitrifier denitrification (Wrage et al. 2001), and added SO₄²⁻ has no effect on N₂O fluxes which means a weak DNRA process (Gardner et al. 2006). N₂O is not a known intermediate of the anaerobic ammonium oxidation (ANAMMOX) process as opposed to the denitrification process (Kartal et al. 2011). Although the genetic potential of nitrous oxide reduction in ANAMMOX was found in recent research (e.g. Ligi et al. 2015), the linkage between ANAMMOX and mitigation of N₂O emission should be further examined to determine a potential role of ANAMMOX in the mitigation of N₂O emission (Zhu et al. 2013). Coupled nitrification-denitrification, which can produce a certain amount of N₂O under low DO condition without NO₃⁻ added, seems to be a possible production mechanism in the two sites. However, we did not find any significant differences in N₂O effluxes between NH₄⁺ and NO₃⁻ added together and single NH₄⁺ addition, indicating that the coupling between NH₄⁺ and NO₃⁻ is of minor importance in terms of N₂O production. It is therefore reasonable to speculate that nitrification could be the main process of N₂O production in rivers of urbanized areas which have high NH₄⁺ concentration and low DO.

Although the influence of NO₃⁻ on N₂O fluxes was not clear as NH₄⁺ or NH₄⁺ + NO₃⁻ (Fig. 4), and NO₃⁻ had no significant correlation with N₂O fluxes in general (Table 3), there was significant positive correlation with N₂O fluxes in urban site sediments under low DO condition ($R = 0.980$, $p < 0.01$). High concentration of NO₃⁻ can not only enhance the process of denitrification, but may also inhibit the activity of nitrous oxide reductase (Miller et al. 1986), indicating that denitrification cannot be ignored in urban site sediments. Therefore, in sediments of polluted urban rivers, the lower concentration of DO and higher concentrations of NH₄⁺ and NO₃⁻ promote favorable conditions for N₂O production from both nitrification and denitrification. SOC could also be a reason why N₂O concentration was higher at the urban site by providing energy for heterotrophic microbes and the

subsequent formation of an anaerobic micro-environment (Beaulieu et al. 2009). For a better understanding of the relationship between nitrification-denitrification processes and distinguishing the source of N₂O, a more detailed and long-term comparison with isotopologue analysis combined with the metagenomic analysis of the functional genes of denitrification is needed (Mander et al. 2014).

Conclusion

Because of the anthropogenic nitrogen input and water quality deterioration, N₂O fluxes at the sediments-water interface were higher at the urban site than at the suburban site, which showed that the poor water quality of river is conducive to N₂O production in sediments. DO and NH₄⁺ concentrations in river water were the most important factors that affected the fluxes of N₂O at the sediment-water interface and the N₂O concentrations in pore water. Microbes in surface sediments quickly consumed DO in overlying water, and nitrification in the top layer of sediment was the major production mechanism of N₂O in suburban rivers with high NH₄⁺ concentration. While in seriously polluted urban rivers, denitrification and nitrification are the two main processes that produce N₂O. From this study, the water quality parameter of DO might be the most important one to target for improvement to reduce N₂O fluxes in urban rivers. Further investigation should be directed to quantify the relative contribution of nitrification and denitrification on N₂O production in river sediments.

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