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RESEARCH ARTICLE

Spatial and temporal variability in nitrous oxide and methane emissions in urban riparian zones of the Pearl River Delta

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Abstract Spatial and temporal variability in nitrous oxide and methane emissions were quantified in three seasons using closed chambers in three riparian zone locations of three branches of the Pearl River, Guangzhou, China. The sampling sites were selected in a rapidly developing urban area of Guangzhou and represented a pollution gradient. The results show that urban riparian landscapes can be large source areas for CH_4 and N_2O, with fluxes of −0.035 ~ 32.30 mg m^{-2} h^{-1} and −5.49 ~ 37.31 μg m^{-2} h^{-1}, respectively. River water quality, sediment texture, and NH_4-N and NO_3-N concentrations correlated with N_2O and CH_4 emission rates. The riparian zones of the more seriously polluted tributaries showed higher greenhouse gas fluxes than that of the less polluted main stem of the Pearl River. Rain events increased emissions of CH_4 by 6.5 ~ 21.3 times and N_2O by 2.2 ~ 5.7 times. The lower concentrations of heavy metals increased the activity of denitrifying enzymes while inhibited the methane producing pathways. This work demonstrates that rapidly developing urban areas are an important source of greenhouse gas emissions, which is conditioned by various environmental factors.

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Introduction

Atmospheric methane (CH_4) and nitrous oxide (N_2O) concentrations exceed pre-industrial levels by 150 and 20 %, respectively, and continue to increase rapidly (IPCC 2013). Due to the high global warming potential of CH_4 (28–34) and N_2O (298), these gases contribute disproportionately to radiative forcing compared to their concentrations. Many studies have been conducted in a variety of terrestrial and aquatic environments (e.g., mangroves, ponds, peatlands, rivers, wetlands, sewage treatment facilities, rice paddies, dry land agricultural fields, etc.) to evaluate gas emission fluxes and factors regulating CH_4 and N_2O fluxes. These studies indicate that anthropogenic emissions of N_2O represent around 30–45 % of the present-day global emissions and over 60 % of CH_4 emissions (Chen et al. 2010a, b; Stadmark and Leonardson 2007; Stow et al. 2005). Quantification of greenhouse gas (GHG) emissions from different natural landforms has become a priority research topic in China in efforts to generate emission inventories and develop strategies to reduce greenhouse gas emissions (Garg et al. 2012).

There is great interest in quantifying greenhouse gas fluxes from riparian zones in estuarine areas as they may represent landscape hotspots for reduced greenhouse gas emissions. Mangrove sediments can act as sources of the greenhouse trace gases, nitrous oxide (N_2O) and methane (CH_4) (Allen et al. 2011). Lu (1999) studied methane fluxes from sediments in different zones of a *Bruguiera sexangula* mangrove wetland during one whole year period, at Changning River estuary, northeast of Hainan Island, China. The results show that there is great seasonality for methane (CH_4) production,

and different horizontal and vertical patterns occur in different seasons and different zones. Xiang (2009) found distinct space-time variation in N_2O emissions among high, middle, and low tidal flats with different vegetation in Chongming Dongtan (Yangtze River Delta). *Phragmite saustralis* increased the N_2O flux while *Scirpus mariqueter* decreased the N_2O flux. Marinho (Marinho et al. 2004) used diffusion chambers to quantify N_2O fluxes from an alluvial soil in the lower Mississippi River Valley and found that rainfall was an important factor regulating N_2O flux. Beaulieu (Beaulieu et al. 2010) measured N_2O emissions from the water surface and production in sediments and the water column of the Ohio River (nitrogen-enriched river) and found maximum N_2O emissions in the major urban center and strong seasonal variation with higher rates in summer and lower rates in winter. Berryman et al. (2009) studied on restoration of wetland hydrology of the Rice Lake Wetland near the city of Detroit Lakes, Minnesota. The results show that raising the water level in soil cores result in decreased nitrous oxide (N_2O) emissions, increased methane (CH4) emissions, and an overall increase in total global warming potential (GWP).

The Pearl River Delta (PRD) is one of the most developed areas in China accounting for about 10 % of the gross domestic product (GDP) and 4 % of the Chinese population (Huang et al. 2012). Rapid urbanization has resulted in various impacts on the environment, including environmental contamination and ecological damage (Guneralp and Seto 2008; Jiang et al. 2004). Contaminants such as heavy metals (e.g., Cd, Pb, Cu), polycyclic aromatic hydrocarbons (PAHs), nitrogen, and low dissolved oxygen contribute to environmental pollution (Duzgoren-Aydin 2007; Zhang et al. 2012). Surface water quality of the Pearl River has been rapidly deteriorating for the past 15 years. Water quality data from 1984 to 2000 at 9 locations along the Pearl River near Guangzhou indicated that industrial effluents and domestic sewage were the principal sources of pollutants (Dong and Mei 2008). There is a strong positive correlation between the rate of urbanization and the increase of pollution levels in urban rivers of the PRD (Ouyang et al. 2006).

As the interface between terrestrial and aquatic ecosystems, the riparian zone is an important landscape component that is affected by pollution from both terrestrial and aquatic sources. Riparian zones provide several valuable ecosystem services, such as filtering polluted surface and subsurface flows, providing biota with habitat, protecting river banks from erosion, improving the microclimate in rivers and adjacent fields, and providing hydrologic connectivity across the landscape (Mander et al. 2005). Greater attention has been focused on riparian zones due to their importance, especially in the urban environment (Balestrini et al. 2011; Borin et al. 2004; Bradley et al. 2011). Groffman suggested that urban area hydrologic factors could increase the abundance and reduce the consumption of NO_3 in urban area riparian zones, due to a decline in the sink strength for NO_3 through denitrification and biotic uptake (Groffman et al. 2002). Riparian zones are a potential hot spot for greenhouse gas emissions because they possess many of the conditions (e.g., anoxic, high organic matter) required for producing reduced greenhouse gases (Freeman et al. 1997). Using constructed riparian ecosystems to improve river water quality and reduce non-point source pollution is now an important strategy utilized in several cities of the PRD. Previous research suggests that appropriately designed constructed wetlands in riparian zones could emit less methane than natural wetlands, while providing a significant nutrient sink (Fink and Mitsch 2007; Mitsch et al. 2008; Sha et al. 2011). Among design criteria, many sediment parameters have been found to influence greenhouse gas production, such as temperature, water-filled pore space, redox potential (E_h), organic matter quantity and quality, and microbial activity (O'Connor and Hondzo 2008). However, little is currently known about the action of heavy metals on greenhouse gas production in sediments.

This study used closed chambers to measure CH_4 and N_2O fluxes from three riparian zone positions (0, 5, and 10 m from river-land boundary) of three branches of the Pearl River as it flows through the Guangzhou urban area. This segment of the Pearl River has the highest urbanization level in the PRD and a large amount of waste water discharges directly to the Pearl River. Nitrous oxide and methane emission fluxes were measured during three seasons (spring, summer, and winter), and associated sediment/soil parameters were measured at the same time. The primary objectives of this study were (i) to quantify CH_4 and N_2O emission fluxes from three riparian ecosystems having different pollution levels; (ii) to examine seasonal differences in CH_4 and N_2O emission fluxes; (iii) to determine the role of heavy metal contaminants in riparian zone soil/sediment and river waters on CH_4 and N_2O emission fluxes; and (iv) to provide reference levels of CH_4 and N_2O emission fluxes in the PRD for developing GHG reduction strategies. Results of this study will provide important design information for developing riparian zone constructed wetlands to enhance water quality in urban areas.

Materials and methods

Sites description

Soil, water and gas samples were collected from the riparian zone of three urban waterways that were branches of the Pearl River which flows through Guangzhou, China (Dong and Mei 2008). Guangzhou has a subtropical climate characterized by hot, humid summers and dry, cool winters. Mean annual temperature is 21.9 °C, relative humidity (RH) is 72–80 %, and mean annual rainfall is 1697 mm (Tao et al. 2011). The summer and winter seasons dominate the year while the transitional seasons, spring and autumn, are particularly short.

Following an intensive field investigation, sampling sites were selected along two tributaries and the main stem of the Pearl River flowing through the Guangzhou urban area. All sites experienced small tidal fluctuations. The sites will be referred to as Chebei River (CR), Tai River (TR), and Pearl River main stem at Guangzhou Higher Education Mega Center (PRM). At each sampling site, a transect consisting of three locations across the riparian zone were established perpendicular to the river (Fig. 1). Chebei River is located in the Tianhe district, the downtown area of Guangzhou. At the CR sampling site, the river bed was covered with black sediment having a sulfide smell, and the waterfront consisted of a wetland with an artificial green belt beginning about 5 m from the river edge. Most parts of the river bank in the vicinity of the sampling area consisted of residential or business land use. The Tai River is located in the Haizhu district, a rapidly developing area of Guangzhou. At the TR site, the riverbed was covered with black sediment having a sulfide smell. The waterfront was covered by hydrophytes with grassland and orchards adjacent to the riparian zone. The main stem Pearl River at the Guangzhou Higher Education Mega Center is located in Panyu district, which is a newly developed area in Guangzhou. The riverbed was covered by sandy sediment which was submerged at high tides. A large area of semi-artificial vegetation (grasses and trees) was distributed along the PRM river bank.

The Chebei River was the most seriously polluted among the three river branches followed by the Tai River and Pearl River main stem. NH_4-N, total *N*, and total *P* at CR were significantly higher than the other two rivers (Table 1). Nitrogen was a major pollutant in the river which was primarily in the form of NH_4 and contributed to low dissolved oxygen concentrations. NH_4-N and TN concentrations of most water samples exceeded the water quality standard of 2.0 mg l^{-1} based on China's national surface water quality standard, level V(GB3838-2002), only suitable for irrigation and landscape. The highest multiple of surpassed factors NH_4-N and TN reached 10 times above the standard limit.

Experimental design

Seasonal sampling campaigns were undertaken on May 19 (spring), July 27 (summer) and December 11, 2011 (winter) and had average daily temperatures of 25, 30 and 11 °C, respectively. All sample collection was conducted between 7 to 10 am during low tide (Allen et al. 2007). A rainy day collection was made on August 9, 2011 to examine the effects of rainfall on emission fluxes and had an average daily temperature of 28 °C and 8 mm of rainfall. The rainy day emission fluxes were conducted at the TR site (intermediate pollution level) from 7 to 10 a.m., and data were compared to the July 27, 2011 (non-rainy day) data from the same site.

At each site, three locations across the riparian zone were established perpendicular to the rivers. Location ① was set at the river water boundary and represented the interface between the riparian buffer and the river water, which stood for lowland; this location was submerged at mean water level. Location ② was set about 5 m away from the river water boundary and represented the transitional area between the river water and dry upland, which stood for midland; this location was submerged only at high water levels. Location ③ was set about 10 m away from the river water boundary and represented the dry upland area, which stood for upland soils; this location did not experience river water inundation.

Measurements of sediment parameters

Soil/sediment samples (0~20 cm) were taken adjacent to the closed chambers at each location every sampling time. A mixed 1 kg sediment sample was sealed in a plastic bag, transported to the laboratory on ice, and then kept refrigerated (≤4 °C) through completion of analyses. Field moist samples were used to determine the water, lipid-P, KCl-extractable CH_4 and N_2O, and particle-size content. The water and lipid-P measurements were made immediately upon return to the laboratory. A subsample was air dried and gently ground to pass a 2-mm sieve for TN and TP analyses. A separate air-dried subsample was ground using an agate mortar to pass a 0.149-mm sieve for total organic carbon (TOC) and heavy metal analyses. All parameters were analyzed according to the "Standard methods of Soil and Agricultural Chemistry Analysis" (in Chinese, 3rd edition) with the following exceptions for phospholipid (lipid-P) analysis to characterize the microorganism community (Yu et al. 2002), and sediment texture was determined by the hydrometer method according to the USDA soil texture classification system (http://www.nrcs.usda.gov/wps/portal/nrcs/detail/soils/). Heavy metals (As, Cd, Cr, Pb, Cu, Zn) in soil/sediment samples were quantified following acid digestion in concentrated nitric acid+hydrofluoric acid+perchloric acid using atomic absorption spectrometry (AAS) (ditto).

Measurements of gas fluxes

The closed chamber technique was used to determine CH_4 and N_2O emission fluxes (Griffith et al. 2002). One static closed chamber was placed at each of the three riparian zone locations (0, 5, and 10 m from river water boundary). The closed chambers were made of PVC pipe (inner diameter 20 cm; outer diameter 20.5 cm; height 30 cm) and covered with aluminum foil to prevent excessive warming; a sealed vent tube at the top of the chamber was used for gas collection. The chambers were inserted 5 cm deep into the soil, and gas samples were collected after 1, 2, and 3 h (Chen et al. 2012). Before taking a gas sample, gas in the chamber was mixed

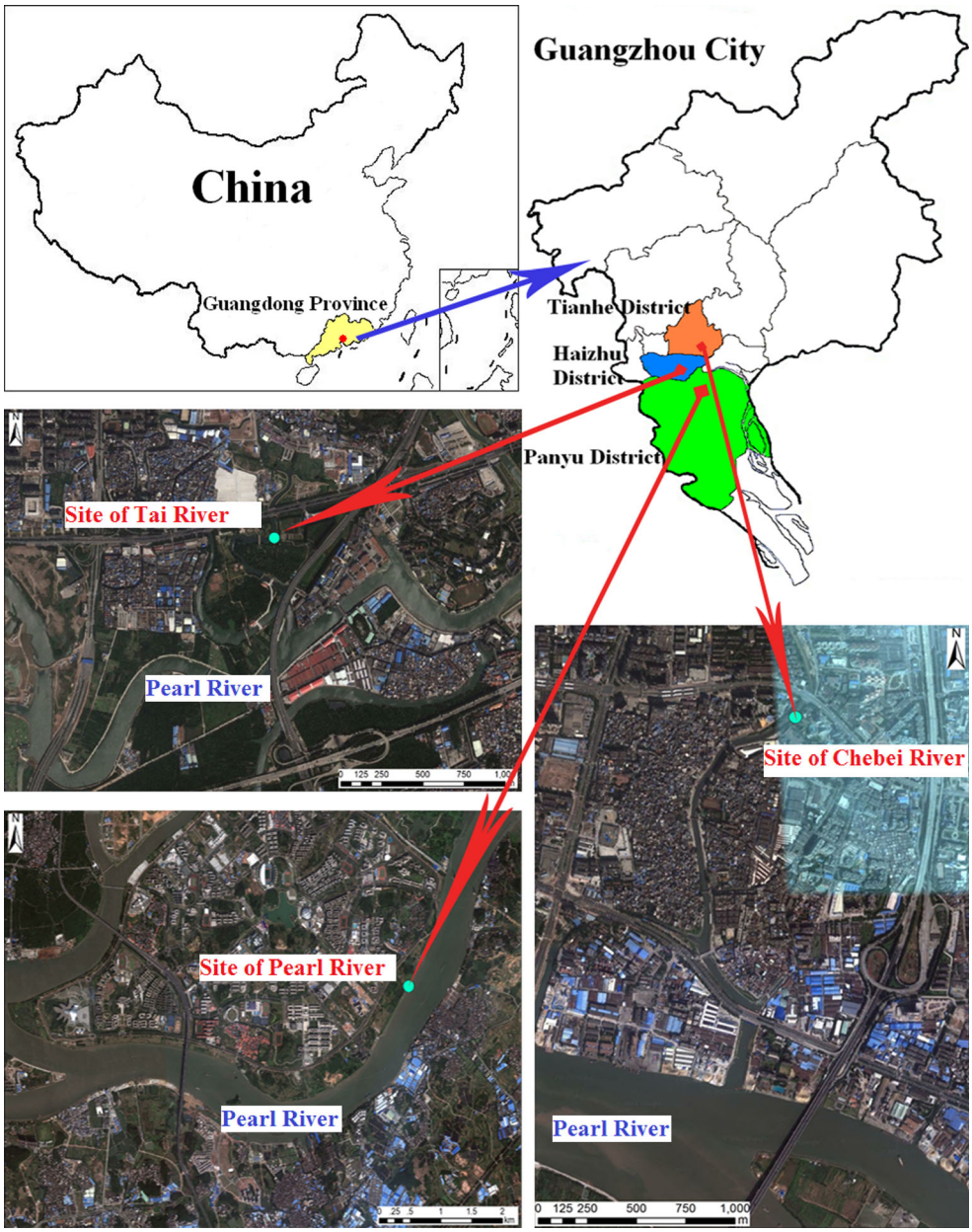

Fig. 1 Sampling campaigns were undertook in three riparian zones. Chebei River (CR), Tai River (TR), and Pearl River main stem at Guangzhou Higher Education Mega Center (PRM)

using a 30-ml syringe; then, a 1-ml gas-tight syringe was used to take a gas sample that was transferred and stored in a gas-tight vial with ambient air (Labco Limited, High Wycombe UK, 5.9 ml) (Laughlin and Stevens 2003). Four replicate gas samples were taken at each collection time: two for CH_4 and two for N_2O analysis. Samples were stored at

Table 1 Quality of river water (mg l^{-1}) at sampling sites

Sampling sites	NH_4-N	NO_3-N	TN	TP	TSS
CR	22.20±7.46	0.54±0.34	22.48±7.88	1.71±1.54	16±1.41
TR	4.90±1.06	1.66±1.60	10.19±1.99	0.35±0.31	18±0.71
PRM	1.55±1.19	1.45±0.59	5.09±2.83	0.56±0.79	23±2.83
Standard level V[a]	2.0	–	2.0	0.4	–

CR Chebei River, *TR* Tai River, *PRM* Pearl River main stem, *TN* total nitrogen, *TP* total phosphorus, *TSS* total soluble solid

[a] China's national surface water quality standard (GB3838-2002)

ambient temperature in the dark until completion of analysis within 48 h. Each sample was taken 2 ml mixed gas from the vial for analysis. All samples were analyzed using gas chromatography (HP 5890, series II) to quantify CH_4 and N_2O concentrations simultaneously. Detailed conditions for GC quantification were as follows: stainless steel pre-column and analytical column with Porapak Q (80~100 mesh); flame ionization detector (FID) (for CH_4) and electron capture detector (ECD) (for N_2O) operated at 200 and 330 °C, respectively; column temperature at 55 °C; N_2 as carrier gas and H_2 as light gas; and standard calibration gases at 3.52 ppm and 328 ppb for CH_4 and N_2O, respectively. N_2O and CH_4 fluxes (F, g/m^2.h) were calculated according to the following equation:

$$F = \frac{M}{V0} \times \frac{P}{P0} \times \frac{T0}{T} \times H \times \frac{dc}{dt}$$

- M Molar mass of N_2O and CH_4 (g mol^{-1}), N_2O: 44, CH_4: 16
- P Air pressure of sampling sites (Pa)
- T Temperature of sampling sites (K)
- H Height from ground to the top of chamber (cm)
- V_0 Molar volume of N_2O and CH_4 at standard state (ml mol^{-1}), 22.4*10^3 ml mol^{-1}
- P_0 Air pressure at standard state (Pa)
- T_0 Absolute temperature at standard state (K)
- $\frac{dc}{dt}$ variation in slope of N_2O and CH_4 concentration over sampling period, mg/L h.

In figures, the unit of N_2O was showed as μg/m^2 h (=F*10^6), and CH_4 was showed as mg/m^2 h (=F*10^3), respectively.

Statistical analysis

Statistical analyses were performed using SPSS 18.0. Statistically significant differences between seasons were calculated by Dunnett's T3 ANOVA using a $p \leq 0.05$ confidence level.

Results

Methane and nitrous oxide emissions

CH_4/N_2O emissions among sites and locations

ANOVA results indicated significant differences ($p<0.05$) in CH_4 emissions among sites, locations, and seasons (Table 2). CH_4 emissions were consistently the highest at CR (the most polluted site) location ① ranging from 9.9 to 32.3 mg m^{-2} h^{-1} compared to values of 0.4 to 3.5 mg m^{-2} h^{-1} at TR and 0.4 to 4.1 mg m^{-2} h^{-1} at PRM. At all sites, location ① at the edge of the river water had the highest CH_4 emissions ($p<0.05$), while fluxes were generally similar and lower (<0.5 mg m^{-2} h^{-1}) at locations ② and ③. A small negative CH_4 flux, indicating CH_4 consumption, occasionally occurred at location ③.

ANOVA results indicated significant differences ($p<0.05$) in N_2O emissions among sites, locations, and seasons like CH_4 (Table 3). Compared to CH_4 emissions, N_2O emissions were more similar in magnitude among the three sites (CR=−3.97~37.3; TR=3.53~30.0; PRM=−5.49~24.9 μg m^{-2} h^{-1}; Fig. 2d~f). Among riparian zone locations, N_2O emissions from location ① at the edge of the river water were higher ($p<0.05$) than higher elevation locations ② and ③. Some negative fluxes were observed at locations ② and ③ indicating that these sites occasionally acted as a sink for N_2O.

Seasonal CH_4 and N_2O emissions

Across seasons, spring CH_4 emissions were generally higher, except for location ① of TR and PRM where CH_4 emissions were the highest in winter (Fig. 2a~c). A small CH_4 sink was occasionally found in summer and winter at location ③ but not in spring.

N_2O emissions tended to have more variable seasonable patterns than observed for CH_4 (Fig. 2d~f). The bars showing different letters (a, b, c, d) indicated significant differences ($p<0.05$). Site CR showed a N_2O emission trend of spring> summer>winter, while PRM showed the lowest N_2O emission fluxes in the summer with higher fluxes in spring and winter. In contrast, site TR showed no consistent seasonal pattern across locations, although the highest flux was observed in spring at location ①.

CH_4 and N_2O emissions response to rainfall

CH_4 and N_2O emissions from all riparian zone locations of TR were generally significantly higher on rainy days (Fig. 3a~b). The bars showing different letters (a, b, c, d) indicated significant differences ($p<0.05$). Emissions decreased from location ① to ③ during both rainy and non-rainy days. CH_4 emissions were 6.5 to 21.3 times greater on the rainy day, while N_2O emission were 2.2 to 5.7 times greater on the rainy day.

Sediment/soil properties and relationships with gas emissions

Soil characterization data for the sediment/soil samples at each site/location are listed in Table 4. Particle-size analysis showed a wide range of textural classes ranging from silt loams to sands (Table 5). All sites had elevated heavy metal

Table 2 Multi-way ANOVA results of the emissions of CH_4

Source	Type III sum of squares	*df*	Mean square	*F*	Sig	Partial eta square	Noncentral parameters	Observed power[b]
Calibration model	2264.05[a]	26	87.08	473.73	0.00	0.99	12316.92	1.000
Intercept	327.04	1	327.04	1779.18	0.00	0.98	1779.18	1.000
Season	75.56	2	38.279	208.23	0.00	0.94	416.49	1.000
Sites	320.26	2	160.13	871.14	0.00	0.98	1742.28	1.000
Location	591.00	2	295.50	1607.58	0.00	0.99	3215.17	1.000
Season+sites	150.32	4	37.58	204.44	0.00	0.97	817.76	1.000
Season+location	131.18	4	32.795	178.41	0.00	0.96	713.65	1.000
Sites+location	674.63	4	168.66	917.53	0.00	0.99	3670.13	1.000
Season+sites+location	320.10	8	40.01	217.68	0.00	0.98	1741.43	1.000
Error	4.963	27	0.18					
Total	2596.06	54						
Corrected total	2269.01	53						

[a] *R* square=0.998 (adjusted *R* square=0.996)

[b] Calculation results of alpha=0.05

concentrations with Cr, Cu, Pb, and Zn concentration lower than level III standard values of the Chinese National Environmental Quality Standard for Soils (GB15618-1995). Concentrations of arsenic and cadmium were 7~8 and 1.5~4 times higher than the level III standard values, respectively (Table 6). All data are average of 3 seasons.

All the measured soil/sediment parameters were used in a stepwise multiple regression analysis to explore for independent parameters that might significantly account for variations in CH_4 and N_2O emissions (Table 7). This regression analysis indicated that NH_4-N was significantly ($p<0.05$) related to increased emissions of both CH_4 and N_2O emissions. The water ratio was also significantly ($p<0.05$) related to CH_4 emissions.

Discussion

Effect of sediment/soil properties on CH_4 and N_2O emission

Sediment/soil texture and water content are two variables that often have a strong effect on CH_4 and N_2O production. Texture exerts an indirect effect through its influence on other

Table 3 Multi-way ANOVA results of the emissions of N_2O

Source	Type III sum of squares	*df*	Mean square	*F*	Sig	Partial eta square	Noncentral parameters	Observed power[b]
Calibration model	7839.38[a]	26	301.51	7.01	0.00	0.87	182.14	1.00
Intercept	4916.19	1	4916.19	114.2	0.00	0.81	114.22	1.00
Season	1282.28	2	641.14	14.89	0.00	0.53	29.79	0.99
Sites	308.61	2	154.30	3.58	0.04	0.21	7.17	0.61
Location	3738.51	2	1869.25	43.43	0.00	0.76	86.86	1.00
Season+sites	1286.07	4	321.52	7.47	0.00	0.53	29.88	0.99
Season+location	344.79	4	86.19	2.00	0.12	0.23	8.01	0.52
Sites+location	192.79	4	48.19	1.12	0.37	0.14	4.48	0.30
Season+sites+ Location	686.34	8	85.79	1.99	0.09	0.37	15.95	0.69
Error	1162.12	27	43.04					
Total	13917.68	54						
Corrected total	9001.49	53						

[a] *R* square=0.871 (adjusted *R* square=0.747)

[b] Calculation results of alpha=0.05

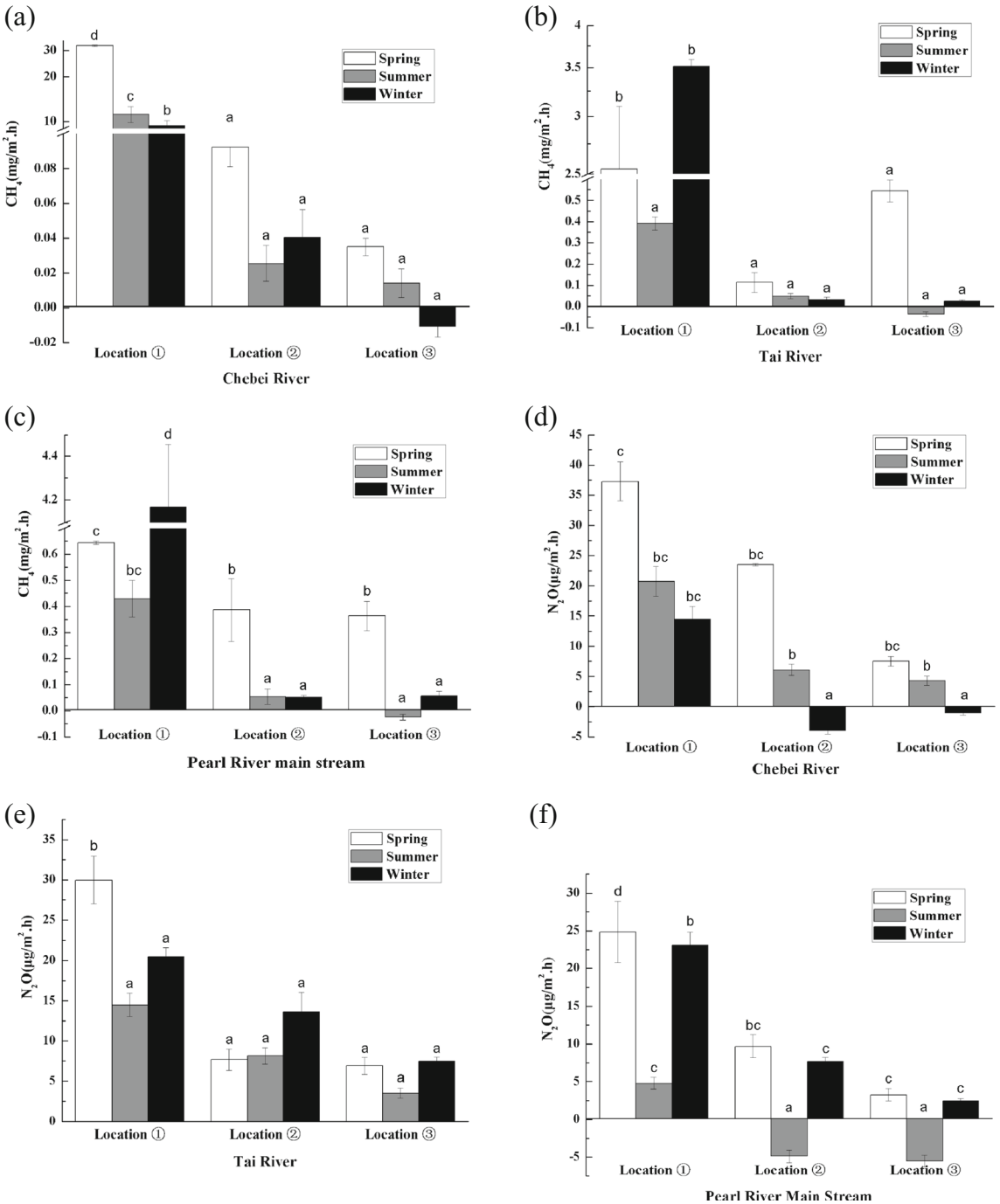

Fig. 2 CH_4 and N_2O fluxes measured at 1 h interval in spring (May 19), summer (July 27), winter (December 11) of 2011, in three locations of three riparian zones (CR, TR, and PRM). The *bars* showing different letters (**a**, **b**, **c**, **d**) indicate significant differences ($p<0.05$)

parameters such as water ratio, Eh, and soil/sediment fertility. In this study, sites with higher sand contents had lower N_2O emission compared with those sites having higher silt and clay contents. Finer texture sediments maintain higher water and organic matter contents that lead to a better environment for anaerobic and facultative microorganisms that are responsible for denitrification. In contrast, CH_4 emissions were higher for those sites having higher sand contents. Research results from Cai Zu-cong (Cai et al. 1998) found similar results and attributed the effect to high silt and clay contents maintaining a higher Eh (more strongly poised with Mn, Fe, and S compounds) and occluding more CH_4 due to slower diffusion through micropore-dominated soils.

Among the various heavy metals, arsenic and cadmium had the highest concentrations and posed the greatest toxicity threat in the experimental riparian zones in the PRD urban

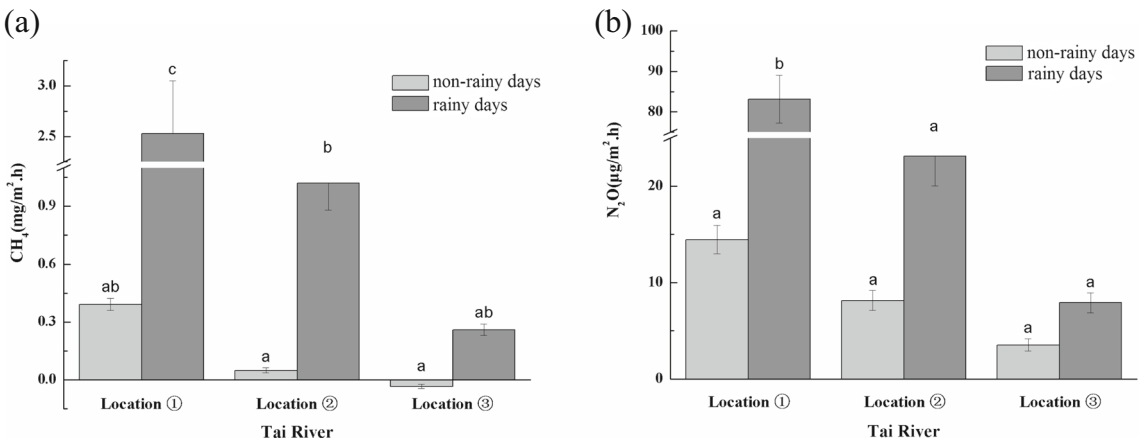

Fig. 3 CH_4 and N_2O fluxes measured at 1 h interval in a rainy day of summer (August 9, 2011), in three locations of TR zone. The *bars* showing different letters (**a**, **b**, **c**, **d**) indicate significant differences ($p<0.05$)

area. In addition to microbial toxicity effects, lower concentrations of heavy metals (e.g., Cu, Pb, As, Cd) have been shown to increase the activity of denitrifying enzymes while high heavy metal concentrations inhibited denitrifying enzyme activities so that the concentration of ammonium in the sediment-water environment may increase and the removal of nitrate may be reduced or even enhance the release of N_2O (Magalhaes et al. 2007; Sakadevan et al. 1999). Based on the regression results shown in Table 7, most heavy metals (except for As) were inversely related with CH_4 emission, suggesting a potential inhibition of methane producing pathways. In contrast, all heavy metals displayed a positive relationship with N_2O emissions suggesting a promotion of the denitrification process, which may be a kind of stress reaction to denitrification. These results suggest that further studies of heavy metal pollution on CH_4 and N_2O production rates are warranted. In situ incubations of cores injected with various levels and ratios of heavy metals may provide important mechanistic information relevant to methanogenesis and denitrification dynamics in soils and sediment contaminated with heavy metals in rapidly developing urban areas.

Previous studies have confirmed a strong relationship between CH_4 emission and water ratio and organic matter (Christiansen et al. 2012). The decreasing trend of CH_4 fluxes from location ①→②→③ was consistent with the sediment-water ratio and TOC. For N_2O production, increased NO_3-N can enhance denitrification levels (Esteves et al. 2001; Tortosa et al. 2011); however, N_2O emissions did not correspond to sediment NO_3-N concentrations in our study, possible due to the consumption (depletion) of NO_3^- by denitrification. Bradley (Bradley et al. 1992) found that NO_3-N concentration only accounted for 34 % of the variation in denitrification with organic carbon content being the more important factor. Similarly, Desimone (Desimone and Howes 1996) demonstrated that organic carbon was the major limitation in regulating denitrification versus NO_3^- transport processes in a coastal aquifer. In our study, those sites with higher organic carbon content tended to have higher N_2O emissions. The

Table 4 The characteristics of soil/sediment samples

Sites and locations		NO_3-N (mg kg^{-1})	NH_4-N (mg kg^{-1})	TN (g kg^{-1})	TP (g kg^{-1})	Lipid-P (nmol P g^{-1})	TOC (%)	Water ratio (%)
CR	①	0.74±0.84	5.11±4.06*	1.78±1.73*	0.57±0.47	36.04±31.43*	2.22±1.13	45.5±11.7*
	②	7.54±5.80*	1.91±1.80	0.29±0.26	0.54±0.42	21.37±23.55	0.74±0.54	13.1±6.4
	③	0.76±0.71	1.29±1.53	0.25±0.13	0.42±0.09	7.00±1.21	0.93±0.16	7.0±6.8
TR	①	1.65±1.78	2.42±1.05	2.55±0.25*	0.66±0.57	35.25±32.32*	5.21±1.50*	55.2±5.2*
	②	10.0±4.58*	1.41±1.52	1.63±0.46*	0.79±0.58	17.24±14.38	3.78±0.14	32.8±8.9
	③	5.11±1.56	1.70±1.40	0.88±0.21	0.36±0.10	12.76±6.37	2.16±0.84	16.8±3.8
PRM	①	1.84±1.59	7.64±2.74*	0.72±0.69	0.21±0.29	7.80±1.87	1.59±1.63	21.5±2.3
	②	2.61±1.55	2.81±1.18	1.22±0.41	0.41±0.04	10.07±1.00	3.99±1.95*	19.4±6.5
	③	0.32±0.25	2.47±1.86	0.68±0.28	0.21±0.01	11.59±3.15	1.95±0.72	15.9±2.7

CR Chebei River, *TR* Tai River, *PRM* Pearl River main stem, *TN* total nitrogen, *TP* total phosphorus, *TOC* total organic carbon

*$p<0.05$ level of significance

Table 5 Sediment texture classification of samples[a]

Separates (%)	CR			TR			PRM		
	①	②	③	①	②	③	①	②	③
Sand	82	92	73	19	29	59	86	68	71
Silt	11	1	22	62	52	26	9	25	18
Clay	7	7	5	19	19	15	5	7	11
	Loamy sand	sand	Sandy loam	Silt loam	Silty clay loam	Sandy clay loam	Loamy sand	Sandy loam	Loamy sand

[a] Using hydrometer method and classified according soil texture classification system of the United States of America (USDA)

CR Chebei River, *TR* Tai River, *PRM* Pearl River main stem

river boundary location (①) demonstrated the highest N_2O emissions that may reflect daily tidal cycles that enhance alternating conditions of aerobic and anaerobic conditions, as well as inputs of NO_3 from river water to the anaerobic hyporheic zone. These conditions may contribute to greater NO_3^- availability at the river boundary zone where the availability of NO_3^- appears to be the rate-limiting step in the denitrification process. In contrast, the transitional zone provides a better environment for nitrification given that it experiences less saturation and potentially better aeration (i.e., higher O_2 content) that would subsequently inhibit the denitrification process. As a result, location (②) tended to have higher NO_3-N concentrations; however, the more oxygenated sediments possibly inhibit the production of N_2O by denitrification. Compared to locations ① and ②, the upland position (③) had the lowest water and organic matter concentrations which may limit anaerobic respiration rates and N_2O production.

Spatial variation of CH_4 and N_2O emissions

Most of the tributaries of the Pearl River flowing through urban areas of the PRD are seriously polluted with several different contaminants (e.g., heavy metals, polycyclic aromatic hydrocarbons, nitrogen). As the most seriously polluted stream in this study, CR had the highest CH_4 emissions compared to the other two streams, especially at the water boundary location (①). High NH_4-N concentrations were observed in the experimental river with concentrations >20 mg L^{-1} at CR. Ammonium oxidation requires oxygen, which contributes to low dissolved oxygen levels in water and sediments (Tanner et al. 2002). The depletion of oxygen by NH_4 oxidation in sediments at the river boundary provides a favorable anoxic environment conducive to methanogenic Archaea activity (Chen et al. 2010a, b). In addition, the CR site had sandier sediment textures (sand and loamy sand) suggesting a poorly poised (Eh buffered) system due to low concentrations of iron and manganese oxides/hydroxides. As such, the high NH_4-N concentrations and sandy sediment textures at CR were associated with the highest levels of CH_4 emission. Both TR and PRM had lower NH_4-N concentrations in the stream water (<5 mg L^{-1}) and less sandy sediment textures that may contribute to the lower CH_4 emission rates from these sites.

N_2O emissions from the river boundary locations (①) were the highest among the three locations along the riparian

Table 6 The content of heavy metals in soil/sediment samples (mg•kg^{-1})

Sites and locations		As	Cd	Cr	Pb	Zn	Cu
CR	①	309.4±13.21	1.83±0.61	35.92±10.91	54.45±19.20	181.68±56.65*	105.79±100.78*
	②	310.2±5.31	1.50±0.84	23.86±11.84	47.59±20.29	138.13±74.12	20.2±10.48
	③	310.2±12.53	2.45±0.64	25.03±9.31	116.06±12.39*	90.62±28.13	9.60±2.09
TR	①	318.2±4.91	4.00±0.71*	92.57±20.48*	71.48±13.57	292.87±47.98*	86.65±27.47*
	②	325.3±22.10	4.27±0.52*	90.20±18.75*	74.71±10.39	222.41±31.44*	53.56±11.81
	③	310.60±7.12	2.12±0.42	39.23±7.66	24.42±6.24	65.26±27.08	15.86±5.01
PRM	①	307.3±1.46	2.10±0.05	42.47±3.67	31.45±1.82	126.94±49.35	21.00±1.96
	②	290.2±29.49	2.27±0.12	52.85±3.78	27.13±5.98	72.17±29.83	18.96±9.08
	③	321.4±15.28	3.09±0.93	70.89±18.48*	21.55±0.44	48.79±10.15	11.18±1.43
Standard level III[a]		40	1.0	300	500	500	400

CR Chebei River, *TR* Tai River, *PRM* Pearl River main stem

[a] 《National soil quality standard》 (China, GB 15618–1995)

*$p<0.05$ level of significance

Table 7 Regression analysis of $lnCH_4$/lnN_2O and sediment parameters (significant coefficients are highlighted at the $p<0.05$ (*) level of significance)

	$lnCH_4$		lnN_2O	
	Coefficients	*t*	Coefficients	*t*
NH_4-N	0.516*	3.017	0.181*	2.241
NO_3-N	−0.244	−1.319	0.148	0.527
TN	−0.189	−0.564	0.279	1.093
TP	−0.138	−0.670	0.142	0.521
Water ratio	0.078*	3.007	0.470	2.096
Lipid-P	0.094	0.425	0.386	1.530
TOC	0.362	1.573	0.138	0.507
As	0.002	0.011	0.008	0.030
Cd	−0.234	−1.045	0.080	0.281
Cr	−0.279	−1.263	0.064	0.231
Pb	−0.001	−0.005	0.339	1.320
Zn	−0.386	−1.315	0.449	1.975
Cu	−0.076	−0.226	0.273	1.059
Sand separate (%)	0.313	1.321	−0.232	−0.846
Silt separate (%)	−0.309	−1.313	0.249	0.918
Clay separate (%)	−0.255	−1.096	0.139	0.486

*$p<0.05$

transect. N_2O emissions at the river boundary generally followed CR>TR>PRM, which was similar to the trend in river water NH_4-N concentration, but in contrast with NO_3-N concentrations (Table 1). The lack of a correlation between N_2O fluxes and NO_3-N in water and sediments in this study is in contrast to several other studies. However, the high N_2O production and low NO_3-N concentrations at the river boundary location possibly reflect depletion of NO_3-N by the denitrification process. N_2O production can result from both nitrification and denitrification reactions under aerobic and anoxic conditions, respectively. The very high NH_4-N in the sediments can inhibit both ammonia oxidation and NO_2^- oxidation limiting N_2O fluxes from nitrification reactions (Kim et al. 2006; Yun and Kim 2003). The high river water and sediment NH_4-N concentrations and low NO_3-N concentrations in the three experimental rivers indicate that nitrification was the rate-limiting step in N_2O production (Chen et al. 2006). Since anoxic conditions limit nitrification in the sediments, a more likely source of NO_3-N for nitrification is NO_3-N diffusion from the water column. This is consistent with the higher N_2O emissions at the CR site (especially at the river boundary location) where very sandy sediment textures allow for rapid diffusion of NO_3-N into the sediments and diffusion of N_2O from the sediments.

In our study, the river boundary area accounted for the largest portion of CH_4 and N_2O emissions among the three riparian zone locations. CR and TR were smaller tributaries compared to the main stem of the Pearl River (PRM). Both of the smaller tributaries emitted higher levels of CH_4 and N_2O than the main river site, in part due to the higher levels of nitrogen pollution. Guangzhou is a typical Chinese city experiencing rapid urban development that has resulted in high levels of water pollution. This study demonstrates that these polluted urban waterways can be a large source of the greenhouse gases N_2O and CH_4. Compared to other studies reported in the literature, riparian zones associated with waterways in the urban area of Guangzhou displayed generally higher CH_4 emissions and similar to lower N_2O emissions (Table 8).

Seasonal variation of CH_4 and N_2O emissions

Several aspects of the seasonal variations of gas emissions found in this study are similar to the findings of other studies. Allen (Allen et al. 2007) found that CH_4 emissions dominated in summer and autumn seasons, whereas N_2O emissions dominated in winter. In contrast, there were no marked seasonal patterns or differences between urban grasslands and forests for N_2O emissions in Baltimore, Maryland (Groffman et al. 2009). Our study showed that even though several sediment parameters in summer were similar to or more appropriate for GHG production than in spring, including TN, NO_3-N, and TOC, the CH_4 and N_2O fluxes in the spring season were much higher than in summer. Since different places have different seasonal temperature and sediment characteristics, it is not surprising that maximum CH_4 and N_2O fluxes are found during

Table 8 Comparing of CH_4/N_2O emission fluxes of riparian zone between Guangzhou and other places in China

Locations	CH_4 (mg m^{-2} h^{-1})	N_2O (μg m^{-2} h^{-1})	Time
Xiangxi River in Three Gorges Region (Zhao et al. 2011)	0.2449	11.7	2009.10~2010.10
Chongming east tidal flat in Yangtze estuary (Wang et al. 2007)	6.56	69.9	2004.07~08
Forest soil in Northeast China (Liu et al. 2010)	−0.0154~−0.0315	11.5~19.3	2008.11~2009.05
Fresh mashes in Sanjiang Plain of Northeast China (Song et al. 2006)	−0.35~32.52	−32~150	2002.06~2004.12
Rice paddy of Jiangning district in Nanjing (Zou et al. 2003)	0.63~1.39	169.57~231.48	2001.05~10
Peat Marsh in Zoigê Plateau (Wang 2010)	2.43	20	2003~2005
Riparian zones in Guangzhou (this research)	−0.035~32.30	−5.49~37.31	2011.05~12

different seasons in other studies. Guangzhou has a hot, wet summer and the temperature in summer is often above 30 °C. Most studies have determined higher rates of greenhouse gas production at higher temperatures; however, our study suggests that higher temperature might limit greenhouse gas emissions or other factors, such as TN, NO_3-N, and TOC, are more important in regulating greenhouse gas emissions than temperature. Further study is needed to monitor the greenhouse gas emissions in the area in all spring and summer seasons.

During the rain event at TR, sediment/soil NO_3-N and water ratio increased in locations ② and ③, and CH_4 and N_2O fluxes were significantly higher than fluxes measured on a recent non-rainy day. Though the sediment NO_3-N concentration decreased, there was also a significant increase of CH_4 and N_2O emissions at location ① during the rainy day. Tortosa (Tortosa et al. 2011) also found that rainfall could increase greenhouse gas emissions (CO_2, CH_4 and especially N_2O) on rainy days, but they did not determine a mechanism. One important factor may be that gas exchange by mass flow was initiated by rainfall. As rainfall enters the soil/sediment, the water replaces the gas in the pore space which increases in the gas pressure resulting in the purging of the gases from the soil/sediment pores. Furthermore, rainfall can create anaerobic environment and contains higher OM to enhance methanogenesis and denitrifying activities, which may contribute to increasing greenhouse gas emissions from soil/sediment. Thus, to determine an accurate record of greenhouse gas emissions for an annual budget, it is critical to determine gas emission rates across a wide range of riparian zone locations, seasonal conditions, tidal cycle characteristics, across diel time scales, and during contrasting weather conditions.

Conclusion

There is a critical need to quantify greenhouse gas emissions from rapidly urbanizing areas, such as the Pearl River Delta. Our study showed higher rates of CH_4 emission and similar to lower rates of N_2O emissions from the polluted river networks in the PRD compared to other published studies. This work demonstrates that rapidly developing urban areas are an important source of greenhouse gas emissions and must be taken into account in global inventories of greenhouse gases.

Riparian zones were shown to be net source of methane and nitrous oxide from polluted urban rivers and emissions varied by location (distance from river), seasons, and during rainfall events. The river boundary area (interface between river and land) emitted the highest levels of CH_4 and N_2O compared to transitional riparian and upland areas at increasing distances from the river water edge. When comparing CH_4 and N_2O gas fluxes with site properties, differential flux rates appear to be associated primarily with differences in river water quality (especially NH_4 and NO_3), sediment textures (controlling dissolved oxygen and diffusion rates), and heavy metal concentrations. The hypoxic/anoxic waterways inhibit NH_4-N oxidation and formation of NO_3-N which limit N_2O emissions. In contrast, hypoxic/anoxic waterways and sediments contribute to rapid depletion of terminal electron acceptors contributing to low E_h conditions that favor methanogenesis.

Most of the streams flowing through the Guangzhou urban area are seriously polluted. The Chebei and Tai Rivers, which are two tributaries of the Pearl River, were more seriously polluted resulting in higher level of CH_4 and N_2O emissions than the main stem of the Pearl River. Emission fluxes varied significantly during different seasons with the spring season having the highest CH_4 and N_2O fluxes. Rain events also contributed to a spike in CH_4 and N_2O emissions, possibly due to mass flow induced release of gases from soil/sediment pores by the infiltrating rainfall. The lower concentrations of heavy metals have shown to increase the activity of denitrifying enzymes while inhibited the methane producing pathways. Given the heavy metal contamination prevalent in the PRD, understanding the impact of heavy metals on greenhouse gas emissions from riparian zones remains a critical research need.

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References

Allen D, Dalal RC, Rennenberg H, Schmidt S (2011) Seasonal variation in nitrous oxide and methane emissions from subtropical estuary and coastal mangrove sediments. Aust Plant Biol 13:126–133

Allen DE, Dalal RC, Rennenberg H, Meyer RL, Reeves S, Schmidt S (2007) Spatial and temporal variation of nitrous oxide and methane flux between subtropical mangrove sediments and the atmosphere. Soil Biol Biochem 39:622–631

Balestrini R, Arese C, Delconte CA, Lotti A, Salerno F (2011) Nitrogen removal in subsurface water by narrow buffer strips in the intensive farming landscape of the po river watershed, Italy. Ecol Eng 37:148–157

Beaulieu JJ, Shuster WD, Rebholz JA (2010) Nitrous oxide emissions from a large, impounded river: the Ohio River. Environ sci technol 44:7527–7533

Berryman EM, Venterea RT, Baker JM, Bloom PR, Elf B (2009) Phosphorus and greenhouse gas dynamics in a drained calcareous wetland soil in Minnesota. J Environ Qual 38:2147–2158

Borin M, Bigon E, Zanin G, Fava L (2004) Performance of a narrow buffer strip in abating agricultural pollutants in the shallow subsurface water flux. Environ Pollut 131:313–321

Bradley PM, Fernandez M, Chapelle FH (1992) Carbon limitation of denitrification rates in an anaerobic groundwater system. Environ sci technol 26:2377–2381

Bradley RL, Whalen J, Chagnon PL, Lanoix M, Alves MC (2011) Nitrous oxide production and potential denitrification in soils from riparian buffer strips: influence of earthworms and plant litter. Appl Soil Ecol 47:6–13

Cai ZC, Shen GY, Yan XY, Tsuruta., Yagi H, Minami K (1998) Effects of soil texture, soil temperature and eh on methane emissions from rice paddy fields. Acta Pedol Sin 145–154. (In Chinese)

Chen GC, Tam NFY, Ye Y (2012) Spatial and seasonal variations of atmospheric N_2O and CO_2 fluxes from a subtropical mangrove swamp and their relationships with soil characteristics. Soil Biol Biochem 48:175–181

Chen GY, Cao XY, Song CL, Zhou YY (2010a) Adverse effects of ammonia on nitrification process: the case of Chinese shallow freshwater lakes. Water Air Soil Poll 210:297–306

Chen H, Wu N, Yao SP, Gao YH, Wang YF, Tian JQ et al (2010b) Diurnal variation of methane emissions from an alpine wetland on the eastern edge of qinghai-tibetan plateau. Environ Monit Assess 164:21–28

Chen SL, Ling J, Blancheton JP (2006) Nitrification kinetics of biofilm as affected by water quality factors. Aquacult Eng 34:179–197

Christiansen JR, Vesterdal L, Gundersen P (2012) Nitrous oxide and methane exchange in two small temperate forest catchments-effects of hydrological gradients and implications for global warming potentials of forest soils. Biogeochemistry 107:437–454

Desimone LA, Howes BL (1996) Denitrification and nitrogen transport in a coastal aquifer receiving wastewater discharge. Environ sci technol 30:1152–1162

Dong YJ, Mei YD (2008) The influence of urbanization on the surface water quality in guangzhou. China Rural Water Hydro 48–50. (In Chinese)

Duzgoren-Aydin NS (2007) Sources and characteristics of lead pollution in the urban environment of Guangzhou. Sci Total Environ 385: 182–195

Esteves FA, Enrich-Prast A, Biesboer DD (2001) Potential denitrification in submerged natural and impacted sediments of Lake Batata, an Amazonian lake. Hydrobiologia 444:111–117

Fink DF, Mitsch WJ (2007) Hydrology and nutrient biogeochemistry in a created river diversion oxbow wetland. Ecol Eng 30:93–102

Freeman C, Lock MA, Hughes S, Reynolds B, Hudson JA (1997) Nitrous oxide emissions and the use of wetlands for water quality amelioration. Environ sci & technol 31:2438–2440

Garg A, Shukla PR, Upadhyay J (2012) N_2O emissions of India: an assessment of temporal, regional and sector trends. Clim Chang 110:755–782

Griffith DWT, Leuning R, Denmead OT, Jamie IM (2002) Air-land exchanges of CO_2, CH_4 and N_2O measured by ftir spectrometry and micrometeorological techniques. Atmos Environ 36:1833–1842

Groffman PM, Boulware NJ, Zipperer WC, Pouyat RV, Band LE, Colosimo MF (2002) Soil nitrogen cycle processes in urban riparian zones. Environ sci technol 36:4547–4552

Groffman PM, Williams CO, Pouyat RV, Band LE, Yesilonis ID (2009) Nitrate leaching and nitrous oxide flux in urban forests and grasslands. J Environ Qual 38:1848–1860

Guneralp B, Seto KC (2008) Environmental impacts of urban growth from an integrated dynamic perspective: a case study of Shenzhen, South China. Global Environ Chang 18:720–735

Huang DS, Xu JH, Zhang SQ (2012) Valuing the health risks of particulate air pollution in the Pearl River Delta, China. Environ Sci Policy 15:38–47

IPCC (2013) Summary for Policymakers. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Jiang T, Li K, Ke D (2004) On the water environmental pollution and protection measures in the Guangzhou section of pearl river. J Lake Sci 282-284. (In Chinese)

Kim DJ, Lee DI, Keller J (2006) Effect of temperature and free ammonia on nitrification and nitrite accumulation in landfill leachate and analysis of its nitrifying bacterial community by fish. Bioresour Technol 97:459–468

Laughlin RJ, Stevens RJ (2003) Changes in composition of nitrogen-15-labeled gases during storage in septum-capped vials. Soil Sci Soc Am J 67:540–543

Liu S, Wang CK, Xu F (2010) Soil effluxes of carbon dioxide, methane and nitrous oxide during non-growing season for four temperate forests in northeastern China. Acta Ecologica Sinica 4075-4084

Lu CY, Wong SY, Tam N, Ye Y, Lin P (1999) Methane flux and production from sediments of a mangrove wetland on Hainan Island, China. Mangrove Salt Marshes 3:41–49

Magalhaes C, Costa J, Teixeira C, Bordalo AA (2007) Impact of trace metals on denitrification in estuarine sediments of the Douro River estuary, Portugal. Mar Chem 107:332–341

Mander U, Kuusemets V, Hayakawa Y (2005) Purification processes, ecological functions, planning and design of riparian buffer zones in agricultural watersheds. Ecol Eng 24:421–432

Marinho EVA, DeLaune RD, Lindau CW (2004) Nitrous oxide flux from soybeans grown on Mississippi alluvial soil. Commun Soil Sci Plan 35:1–8

Mitsch WJ, Zhang L, Fink DF, Hernandez ME, Altor AE, Tuttle CL et al (2008) Ecological engineering of floodplains. Ecohydrol Hydrobiol 8:139–147

O'Connor BL, Hondzo M (2008) Response to comment on "enhancement and inhibition of denitrification by fluid-flow and dissolved oxygen flux to stream sediments". Environ sci technol 42:8611–8612

Ouyang TP, Zhu ZY, Kuang YQ (2006) Assessing impact of urbanization on river water quality in the Pearl River Delta economic zone, China. Environ Monit Assess 120:313–325

Sakadevan K, Zheng H, Bavor HJ (1999) Impact of heavy metals on denitrification in surface wetland sediments receiving wastewater. Water Sci Technol 40:349–355

Sha C, Mitsch WJ, Mander U, Lu JJ, Batson J, Zhang L et al (2011) Methane emissions from freshwater riverine wetlands. Ecol Eng 37:16–24

Song CC, Zhang LH, Wang YY, Zhao ZC (2006) Annual dynamics of CO_2, CH_4 and N_2O emissions from freshwater marshes and affected by nitrogen fertilization. Environ Sci 2369–2375

Stadmark J, Leonardson L (2007) Greenhouse gas production in a pond sediment: effects of temperature, itrate, acetate and season. Sci Total Environ 387:194–205

Stow CA, Walker JT, Cardoch L, Spence P, Stow CA (2005) N_2O emissions from streams in the Neuse River watershed, North Carolina. Environ sci technol 39:6999–7004

Tanner CC, Kadlec RH, Gibbs MM, Sukias JPS, Nguyen ML (2002) Nitrogen processing gradients in subsurface-flow treatment wetlands—influence of wastewater characteristics. Ecol Eng 18:499–520

Tao YB, Zhong LJ, Huang XL, Lu SE, Li Y, Dai LZ et al (2011) Acute mortality effects of carbon monoxide in the Pearl River Delta of China. Sci Total Environ 410:34–40

Tortosa G, Correa D, Sanchez-Raya AJ, Delgado A, Sanchez-Monedero MA, Bedmar EJ (2011) Effects of nitrate contamination and

seasonal variation on the denitrification and greenhouse gas production in la Rocina stream (Donana National Park, sw Spain). Ecol Eng 37:539–548

Wang DQ, Chen ZL, Wang J, Xu SY, Yang HX, Chen H, et al. (2007) Fluxes of CH_4 and N_2O from yangtze estuary intertidal flat in summer season. Geochimica 78–88

Wang DX (2010) Emission fluxes of carbon dioxide, methane and nitrous oxide from peat marsh in zoigê plateau. . Wetland Science:220–224

Xiang SL (2009) The emission of N_2O from the Chongming Dongtan wetland under different plants [Master]:East China Normal University. (In Chinese)

Yu X, Zhang XJ, Wang ZS (2002) Biomass examination by lipid-p method for drinking water bio-treatment. Water Wastewater Eng 1–5. (In Chinese)

Yun HJ, Kim DJ (2003) Nitrite accumulation characteristics of high strength ammonia wastewater in an autotrophic nitrifying biofilm reactor. J Chem Technol Biotechnol 78:377–383

Zhang K, Liang B, Wang JZ, Guan YF, Zeng EY. (2012) Polycyclic aromatic hydrocarbons in upstream riverine runoff of the pearl river delta, china: an assessment of regional input sources. Environ Pollut 167:78–84

Zhao Y, Zheng YN, Wu BF, Wang Q, Yuan C, Xu ZR (2011) Observation on greenhouse gas emissions from Xiangxi River in three gorges region. Adv Water Sci 546–553

Zou JW, Huang Y, Zong LG, Zheng XH, Wang YS (2003) A field study on CO_2, CH_4 and N_2O emissions from rice paddy and impact factors. Acta Sci Circumst 758–764