

# Urbanization in China changes the composition and main sources of wet inorganic nitrogen deposition

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**Abstract** Nowadays, nitrogen (N) deposition has become a growing global concern due to urbanization activities increasing the large amount of reactive N in the atmosphere. However, it remains unclear whether urbanization affects the composition and main sources of N deposition in rapidly urbanizing areas such as in China. One-year measurement of wet inorganic N deposition was conducted using ion-exchange resin (IER) columns in the range of 260 km from urban to rural areas in the Pearl River Delta (PRD) region, south China. An increasing pattern of wet inorganic deposition along the urbanization gradient was observed and it increased in the order: rural ( $15.26 \pm 0.20 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ) < suburban/rural ( $21.45 \pm 3.73 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ) < urban ( $31.16 \pm 0.44 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ) < urban/suburban sites ( $34.15 \pm 5.73 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ). Nitrate N ( $\text{NO}_3^-$ -N) accounted for 53.5–79.1 % of total wet inorganic N deposition, indicating a significant negative correlation with distance from the urban core. Based on moss  $\delta^{15}\text{N}$ -values the main source of  $\text{NO}_3^-$ -N was considered to be emitted from vehicles. Our results demonstrate that urbanization has large impacts on the regional pattern of wet inorganic N deposition. Thus, controlling NOx emission, especially vehicle emission will become an effective strategy for N pollution abatement in China.

**Keywords** Urbanization · Nitrogen deposition · Ammonium N · Nitrate N · PRD region

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## Introduction

Formation of reactive nitrogen (N) by anthropogenic activities (Canfield et al. 2010) has been resulting in globally increasing N deposition (Galloway et al. 2008; Peñuelas et al. 2012). N deposition has become an important nutrient supply; however, with its dramatic increase and exceeding critical loads, significant negative effects have to be expected (Matson et al. 1999; Baron et al. 2000; Matson et al. 2002; Manning et al. 2006; Nanus et al. 2012; Baron et al. 2013; Bettez and Groffman 2013), e.g., soil acidification, reduced biodiversity, and plant growth, even on human health through driving the formation of particulate matter and tropospheric ozone (Richter et al. 2005).

Urbanization is one of the most powerful and visible anthropogenic forces on Earth (Dawson et al. 2009), which is characterized by high densities of population and industry. It is accelerating worldwide, with 54 % of the world's population residing in urban areas in 2014 which is expected to reach 60 % by 2050 (UNDESAPD 2014). Urbanization results in high emissions of N-containing pollutants and affects levels of atmospheric N deposition (Lovett et al. 2000; Liu et al. 2008). In cities of Europe (e.g., London) and the USA (e.g., New York), urban areas always received higher rates of N deposition than rural areas (Lovett et al. 2000; Power and Collins 2010), although a decreasing trend of nitrogen deposition was found because of reduced emissions of nitrogen compounds during the past few decades (Galloway and Cowling 2002; Pinder et al. 2011; van der Swaluw et al. 2011).

China has experienced a dramatic and unprecedented increase in urbanization since the initiation of the economic reform in 1978. As a result, reactive N emission from N fertilizers and fossil fuel combustion is also increasing rapidly. Now, China has become by far the largest emitter of reactive N globally higher than the USA and Europe (Liu et al. 2013). Therefore, more attention is paid to China due to its high N deposition (Reay et al. 2008; Elser 2011; Liu et al. 2011; Liu

et al. 2013). A similar pattern of N deposition to Europe and the USA with higher level in cities than in rural was also found (Fang et al. 2011; Huang et al. 2012). Contrast to Europe and the USA, in China, ammonium N ( $\text{NH}_4^+\text{-N}$ ) has been often the main form of N deposition even in cities, which has been mostly attributed to agricultural activities from traditional farming practice (Chen et al. 2004) and excretory wastes (Xiao et al. 2010). Recent studies showed the contribution of nitrate N ( $\text{NO}_3^-\text{-N}$ ) to atmospheric N deposition increases in rapidly urbanizing zones (Zhao et al. 2009; Liu et al. 2013; Wang et al. 2013). In some urban areas,  $\text{NO}_3^-\text{-N}$  already becomes the main form of inorganic N deposition. For example,  $\text{NO}_3^-\text{-N}$  concentration had significantly increased in Shenzhen city over the past 20 years, and its contribution to wet inorganic N deposition increased to 50–63 % during 2001–2006 (Huang et al. 2013). This is due to a drastic increase of  $\text{NO}_x$  emissions from vehicles since 2000 (Streets et al. 2003; Ohara et al. 2007; Xie et al. 2007). However, it is still unknown whether urbanization in China changes the composition and sources of local and regional inorganic N deposition making  $\text{NO}_3^-\text{-N}$  the dominant form of inorganic N deposition.

This paper presents measurements on wet inorganic N deposition at 14 sites along an urbanization gradient in the Pearl River Delta (PRD) region, China. The region has been one area of particular concern due to its fastest speed of urbanization in the world over the past 20 years (Wang et al. 2004) and soaring emission of air pollutants (Wang et al. 2005; Chan and Yao 2008). The objectives of this study were (1) to examine the pattern of wet inorganic N deposition and its composition along the urbanization gradient and (2) to identify the main indicator and sources of wet inorganic N deposition under urbanized conditions.

## Methods and materials

### Description of the study region and sampling sites

The PRD region is adjacent to the South China Sea. It covers an area of  $4.17 \times 10^4 \text{ km}^2$ , hosting more than 4.8 % of the population and contributing about 14.8 % of the gross domestic product (GDP) of China in 2010 (China Statistical Yearbook 2011; Guangdong Statistical Yearbook 1991–2011). Its total emission of anthropogenic  $\text{NH}_3$  reached 582.9 kt in 2010 (Shen et al. 2014), and the number of motor vehicles in this region was more than 9.1 million in 2011 (Shen 2013). It has a typical East Asian monsoon climate. In the hot and humid summer, southwesterly wind from the sea prevails and brings abundant precipitation, while in the relatively cool and dry winter, northeasterly wind from the mainland dominates and brings little precipitation. Its annual

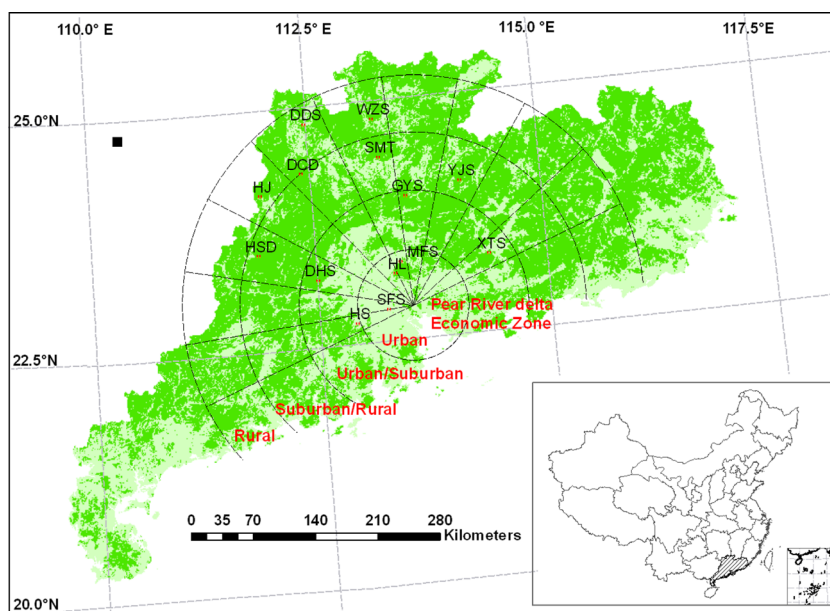
precipitation varies from 1566 to 2133 mm and the mean annual air temperature from 19.65 to 22.22 °C.

An urbanization gradient based on distance from the urban core (Chen et al. 2013) was adopted in this study. Along the prevailing southeast monsoon from Guangzhou City center to the remote mountains of northern Guangdong Province, 14 non-forested sites were chosen in the range of a 260 by 65 km belt transect extending from urban, through urban/suburban and suburban/rural to rural sites. We further divided each class into 10 subzones of equal area. In each class, we semi-randomly chose three or four subzones to locate our sampled sites based on a land-use map. Among the 14 sites, Huolushan, Maofengshan and Shunfengshan, abbreviated to HLS, MFS, and SFS, respectively, belonged to the urban areas; Heshan (HS), Dinghushan (DHS), Guangyinshan (GYS), and Xiangtoushan (XTS) belonged to the urban/suburban areas, Heishiding (HSD), Shimentai (SMT), Yunjishan (YJS), and Dachouding (DCD) belonged to the suburban/rural areas, and Huaiji (HJ), Dadongshan (DDS), and Wuzhishan (WZS) belonged to the rural areas (Fig. 1, Chen et al. 2013). Their longitudes range from  $\text{E}111^\circ 54' 19.78''$  to  $\text{E}115^\circ 21' 54.52''$ , and their latitudes from  $\text{N}22^\circ 46' 0.60''$  to  $\text{N}24^\circ 46' 40.25''$  (Table 1).

### Wet inorganic N deposition

We used ion-exchange resin (IER) columns to quantify inorganic N deposition in bulk precipitation at the study sites. The IER columns were made according to the method developed by Fenn and Poth (2004) and Fang et al. (2011). A funnel was installed on the top of the IER column (a 16 mm  $\times$  330 mm polyvinylchloride (PVC) tube) with a septum and a fitting. A fine mesh screen was placed on the surface of the funnel to keep out debris. The resin used for IER collector is a mixture of strong base styrene anion-exchange resin (201 9 7[717], similar to Amberlite IRA-400) and strong acid styrene cation-exchange resin (001 9 7[732], similar to Amberlite IR-120; Guangzhou, China). Forty grams of mixed resin (half cation and half anion) was added to each PVC column and rinsed with distilled water. At each plot, three to five IER columns were installed to collect precipitation, and two IER columns with both ends sealed were left in each site to determine background N contamination (e.g., potential  $\text{NH}_4^+$  release from amine group from the ion resin, Fang et al. 2011) in the ion resin. The IER columns were set up from January 2011 to June 2011 in the 14 sites, and then retrieved and replaced with a new set every 3 months for four times in every site until June 2012. At the end of each field sampling, the resin columns were unscrewed from the funnel assembly, sealed at both ends, and returned to the laboratory. The  $\text{NH}_4^+\text{-N}$  concentrations were measured by the indophenol blue method followed by colorimetry, and  $\text{NO}_3^-\text{-N}$  concentrations were measured after cadmium reduction to  $\text{NO}_2^-\text{-N}$ , followed by

**Fig. 1** Location of our study sites in Guangdong Province of southern China. A total of 14 open-field sites were selected along the transect (cited from Chen et al. 2013)



sulfanilamide-nicotinamide adenine dinucleotide (NAD) reaction (Liu et al. 1996). Wet inorganic N deposition was calculated using the method adopted by Sheng et al. (2013).

#### Isotope analysis of moss

The moss materials *Haplocladium microphyllum* (Hedw.) at all study sites were collected from January to June 2011. Moss sampling was carried out according to the criteria set by Liu et al. (2007, 2008) that eligible sampling sites should be in

open fields without influences of tree canopy or overhanging vegetation, and samples must be above ground level to avoid surface water splashes, and sites possibly disturbed by domestic animals or pets were also given up. We collected >10 subsamples at each site and merged them into a mixed sample.

Fresh mosses were stored in cleaned plastic bags and transported to the laboratory. Using the treatment method described in Liu et al. (2007), samples were gently rinsed with 1.5 mol L<sup>-1</sup> HCl solution, then washed with deionized water several times (>8 times) until no N (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) was detected in the washed water (using spectrophotometry; limit

**Table 1** Site characteristics

Site (code)	Latitude (N)	Longitude (E)	Distance from urban core (km)	MAP (mm)	MAT (°C)
SFS	22° 49' 7.65"	113° 16' 38.99"	28.0	1742 (351)	22.09 (0.52)
HL	23° 10' 53.30"	113° 23' 2.00"	36.1	1742 (351)	22.09 (0.52)
MFS	23° 18' 5.87"	113° 27' 0.57"	46.7	1742 (351)	22.09 (0.52)
HS	22° 40' 13.31"	112° 54' 14.01"	66.0	1701 (283)	21.15 (0.43)
XTS	23° 18' 26.87"	114° 25' 37.54"	103.8	1730 (340)	22.01 (0.49)
DHS	23° 8' 57.27"	112° 31' 3.07"	107.8	1625 (275)	22.22 (0.47)
GYS	23° 58' 9.34"	113° 33' 49.22"	120.3	2133 (383)	20.95 (0.41)
YJS	24° 4' 55.65"	114° 10' 18.33"	148.6	1758 (314)	19.93 (0.50)
SMT	24° 23' 7.47"	113° 18' 8.49"	167.5	1675 (243)	19.45 (0.43)
HSD	23° 27' 42.85"	111° 54' 19.78"	179.3	1690 (265)	20.99 (0.47)
DCD	24° 16' 58.67"	112° 25' 25.81"	191.0	1597 (328)	19.65 (0.45)
HJ	24° 4' 7.45"	111° 57' 50.40"	207.8	1597 (328)	19.65 (0.45)
WZS	24° 46' 40.25"	113° 15' 28.59"	211.7	1566 (281)	20.38 (0.39)
DDS	24° 46' 17.29"	112° 30' 3.17"	234.5	1597 (328)	19.65 (0.45)

Temperature and precipitation interpolated from nearest meteorological station data. Latitude, longitude, and elevation are from GPS readings taken on sites  
 MAP long-term mean annual precipitation, MAT long-term mean annual temperature

of detection  $<0.005 \text{ mg L}^{-1}$ ). The main purpose of this washing procedure was to remove adsorbed N pollutants. All samples were dried in a vacuum oven at  $65^\circ\text{C}$  and redried after being ground into fine powders using a mortar and pestle.

Moss  $\delta^{15}\text{N}$  were measured on a gas isotope ratio mass spectrometer (Model Finnigan MAT 252). Three replicated measurements per sample were carried out, and values are presented as an average of these measurements. Analysis of potassium nitrate standard ( $\delta^{15}\text{N}=+1.9\text{‰}$ ) was used a standard deviation for  $\delta^{15}\text{N}$ , with a mean  $\delta^{15}\text{N}_{\text{air}}$  value of  $1.9\pm0.2\text{‰}$ . The natural abundance of  $^{15}\text{N}$  was calculated as  $\delta^{15}\text{N}$  values in per mil (‰):  $\delta^{15}\text{N}=[(R_{\text{sample}}/R_{\text{standard}})-1]\times 1000(\text{‰})$ .

## Statistics

One-way analysis of variance (ANOVA) was performed to determine differences in each investigated variable among the four urbanized classes, i.e., urban areas, urban/suburban areas, suburban/rural areas, and rural areas. Linear regression analyses was performed to determine correlations between distance from the urban core and wet inorganic N deposition,  $\text{NH}_4^+-\text{N}$  and  $\text{NO}_3^--\text{N}$  deposition and moss  $\delta^{15}\text{N}$  values. Correlation analysis with two-tail significance test was used to examine the relationships between wet inorganic N deposition,  $\text{NH}_4^+-\text{N}$  and  $\text{NO}_3^--\text{N}$  deposition with moss  $\delta^{15}\text{N}$  values in 14 sites. All analyses were conducted using the SPSS 13.0 for Windows. Statistically significant differences were set at  $P$  values  $<0.05$  unless otherwise stated.

## Results

### Pattern and composition of wet inorganic N deposition

Wet inorganic N deposition ranged from 16.95 to  $47.24 \text{ kg N ha}^{-1} \text{ year}^{-1}$  in the 14 sites and maintained a negative linear relationship with distance from the urban core ( $R^2=0.527$ ,  $P<0.001$ ) (Fig. 2c). The pattern of wet inorganic N deposition along the urbanization gradient showed a decline in the order: urban/suburban ( $34.15\pm5.73 \text{ kg N ha}^{-1} \text{ year}^{-1}$ )>urban ( $31.16\pm0.44 \text{ kg N ha}^{-1} \text{ year}^{-1}$ )>suburban/rural ( $21.45\pm3.73 \text{ kg N ha}^{-1} \text{ year}^{-1}$ )>rural sites ( $15.26\pm0.20 \text{ kg N ha}^{-1} \text{ year}^{-1}$ ) (Fig. 3).

The contribution of  $\text{NO}_3^--\text{N}$  deposition accounted for 53.5–79.1 % and increased significantly along the urbanization gradient similar to the total wet inorganic N deposition (see Fig. 2a,  $R^2=0.688$ ,  $P<0.001$ ). The levels of  $\text{NO}_3^--\text{N}$  deposition at urban and urban/suburban sites were significantly higher than at suburban/rural and rural sites, but there was no significant difference between urban and urban/suburban sites, and between suburban/rural and rural sites. However,

$\text{NH}_4^+-\text{N}$  deposition had no linear relationship with distance from the urban core (see Fig. 2b,  $P>0.05$ ). In comparison with  $\text{NO}_3^--\text{N}$  deposition, the levels of  $\text{NH}_4^+-\text{N}$  deposition were low and showed no significant difference among four urbanized classes (Fig. 3). The ratios of  $\text{NH}_4^+-\text{N}/\text{NO}_3^--\text{N}$  were mostly below 1, and had no significant correlation with distance from the urban core (see Fig. 2d,  $P>0.05$ ).

### Abundance of $\delta^{15}\text{N}$ in mosses

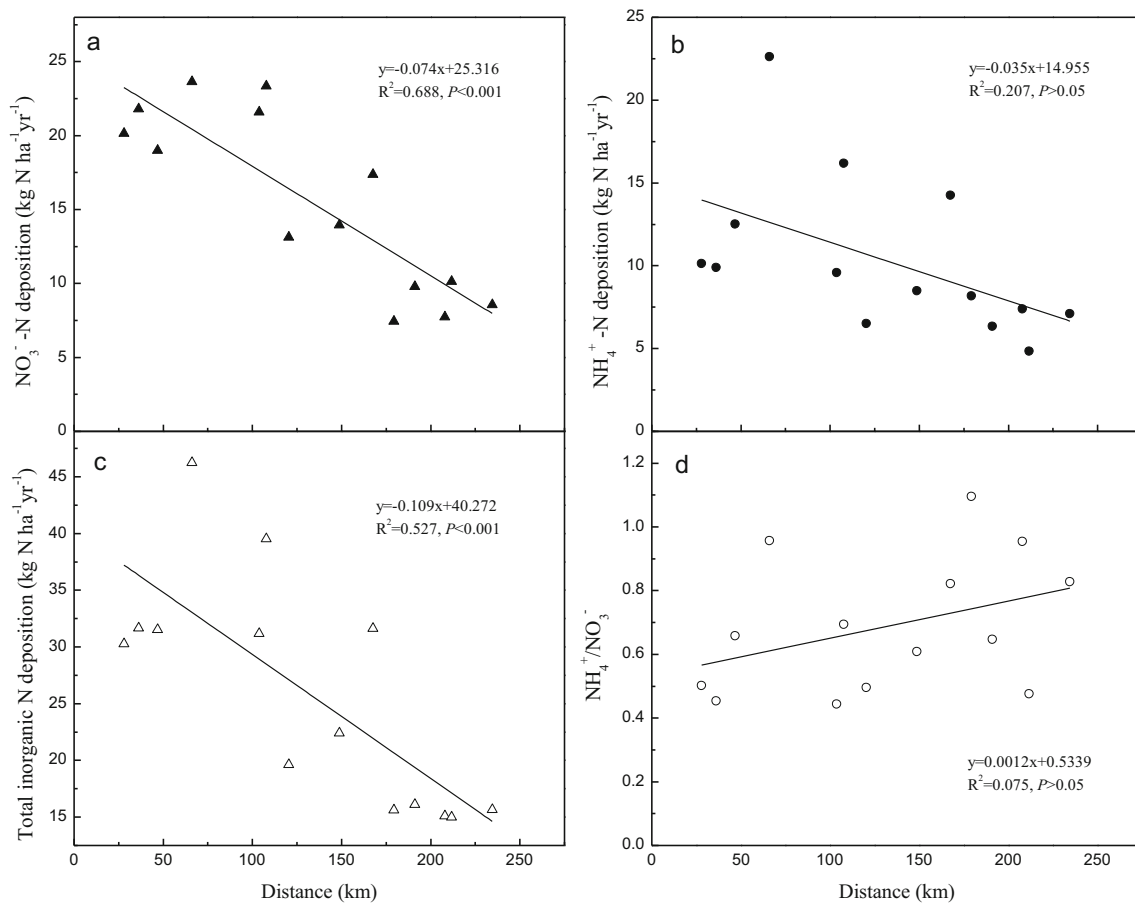
Moss samples showed negative  $\delta^{15}\text{N}$  values and were all in the range of  $0\sim-6\text{‰}$ . There was a positive linear relationship between moss  $\delta^{15}\text{N}$  values and distance from the urban core (see Fig. 4,  $P<0.01$ ). When the data from the 14 single sites were pooled into the four groups, the variation in  $\delta^{15}\text{N}$  values turned out to be highest in urban sites. And the  $\delta^{15}\text{N}$  values in urban and urban/suburban areas were significantly lower than in suburban/rural and rural areas (Fig. 5).

## Discussion

### Pattern and composition of wet inorganic N deposition across the urbanization gradient

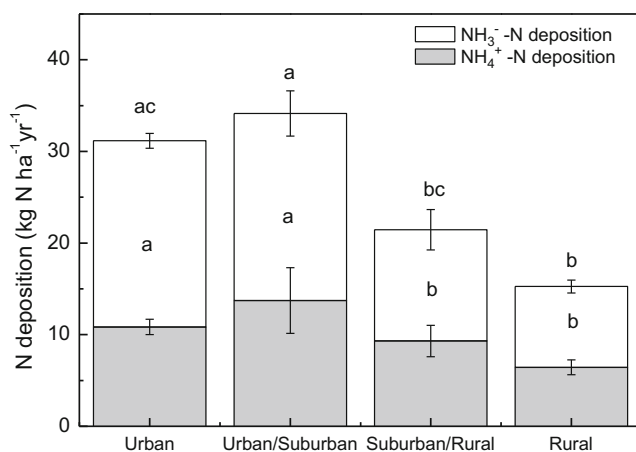
Urbanization impacted the pattern of wet inorganic N deposition with higher levels in urbanized areas (urban and urban/suburban sites) than in non-urbanized areas (suburban/rural and rural sites) (Fig. 3). The trend from urban to rural is similar to those in southern California, southern Poland, and New York City metropolitan area, where N deposition in urban/suburban forests were much higher than in rural forests (Fenn and Bytnerowicz 1993; Bytnerowicz et al. 1999; Carreiro et al. 1999; Lovett et al. 2000; Fang et al. 2011).

The contribution of  $\text{NO}_3^--\text{N}$  to total wet inorganic N deposition exceeded that of  $\text{NH}_4^+-\text{N}$  (Figs. 2 and 3) indicating that  $\text{NO}_3^--\text{N}$  is the dominant component of wet inorganic N deposition. The composition of inorganic N deposition in the PRD region changes our previous view that  $\text{NH}_4^+-\text{N}$  always had been the more important component of inorganic N deposition than  $\text{NO}_3^--\text{N}$  in China (Xu et al. 2001; Chen et al. 2004; Fang et al. 2008, 2009; Cao et al. 2009; Fang et al. 2011). It was well known that China has been an area with high atmospheric  $\text{NH}_3$  deposition (Galloway et al. 1996), mostly attributed to its traditional agriculture, which is an important source of atmospheric  $\text{NH}_3$  by livestock farming and fertilizer application (Schlesinger and Hartley 1992; Zhao and Wang 1994; Galloway et al. 1996). Chen et al. (2004) estimated about 70 % of  $\text{NH}_4^+-\text{N}$  in the deposited N was derived from agriculture. Even in cities, excretory wastes were the main N sources (Xiao et al. 2010). However, our study revealed that the importance of N deposition from

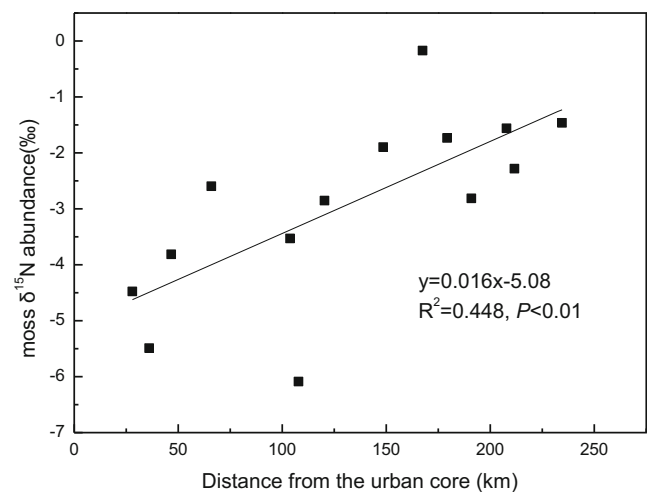


**Fig. 2** Linear relationship between **a**  $\text{NO}_3^-$ -N deposition, **b**  $\text{NH}_4^+$ -N deposition, **c** total wet inorganic N deposition levels, and **d** ratios of  $\text{NH}_4^+$ -N/ $\text{NO}_3^-$  with distances from the urban core. The results of linear

regression analyses and the significance levels ( $P$ ) are shown. In all case, best fit was obtained by linear regression ( $y=a+bx$ ) analysis. Data of 14 samples are indicated

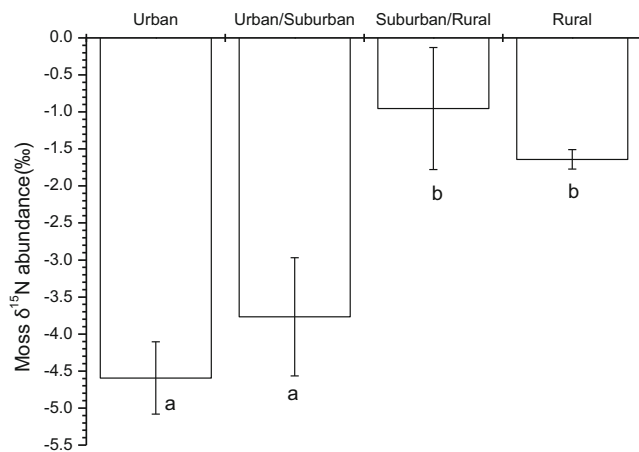


**Fig. 3** The average atmospheric inorganic N depositions among four urbanization gradients. Error bars indicate  $\pm 1\text{SE}$  ( $N=3$  for urban and rural,  $N=4$  for urban/suburban and suburban/rural). Different letters indicate significant differences ( $P \leq 0.05$ ) between gradient classes, and no letters indicate no significant differences ( $P > 0.05$ ) between different urbanization gradient classes, respectively



**Fig. 4** Linear relationship between moss  $\delta^{15}\text{N}$  values with distances from the urban core. The results of linear regression analyses and the significance levels ( $P$ ) are shown. In all case, best fit was obtained by linear regression ( $y=a+bx$ ) analysis. Data of 14 moss samples are indicated





**Fig. 5** Variation in average moss  $\delta^{15}\text{N}$  abundance among different urbanization gradients. Error bars indicate  $\pm 1\text{SE}$  ( $N=3$  for urban and rural,  $N=4$  for urban/suburban and suburban/rural). Different letters indicate significant differences ( $P\leq 0.05$ ) between gradient classes, and no letters indicate no significant differences ( $P>0.05$ ) between different urbanization gradient classes, respectively

urbanization sharply increases, resulting in rapid growth of  $\text{NO}_3^-$ -N emission, and its increasing contribution to atmospheric N deposition (Liu et al. 2013; Wang et al. 2013). Our finding agrees with previous research in Shenzhen city where  $\text{NO}_3^-$ -N accounted for 50–63 % of total wet inorganic N deposition during 2001–2006 (Huang et al. 2013). Similar composition of N deposition was also observed in other rapidly urbanized zones of China, e.g., the Yangtze River Delta Region (Zhao et al. 2009; Liu et al. 2013) and some cities of Europe, e.g., London (Pearson et al. 2000) and Ferrara, Italy (Gerdol et al. 2002). Our results suggested that urbanization enhances  $\text{NO}_3^-$ -N emission and changes the composition of local and regional N deposition.

Distance indicating the levels of wet inorganic N deposition

Distance from the urban core had significant negative correlations with wet inorganic N and  $\text{NO}_3^-$ -N deposition (Fig. 2a, c). Similar result was reported by Power and Collins (2010) from London. Thus, distance from the urban core can be considered as an effective indicator for the levels

of wet inorganic N deposition in rapidly urbanizing regions. The indicative function of distance was further supported by significant positive correlations with soil pH (data unpublished) and organic carbon (Chen et al. 2013) in this region. In other regions, correlations between distance and soil chemical properties (Pouyat et al. 2008) and concentration and fluxes of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{Cl}^-$  in throughfall (Lovett et al. 2000) were also observed. Therein, we demonstrated that distance from the urban core can be an efficient index of urbanization effects.

The decrease in wet inorganic N deposition with distance from the urban core is mostly attributed to the transport and deposition of N-containing pollutants in urbanized areas. The  $\text{NH}_3$  concentration near the ground, and thus the deposition decreases with distance from the source due to dispersion, particle formation and deposition.  $\text{NH}_3$  cannot be transported over very long distance from its source due to its rapid conversion to  $\text{NH}_4^+$  (Asman and van Jaarsveld 1992). Its maximum transport distance only reaches 50 km downwind (van Herk et al. 2003). Given these clues, it was concluded that most of  $\text{NH}_3$  emitted from urban and urban/suburban areas can only be transported to sites not exceeding 50 km distance from the  $\text{NH}_3$  source, which may explained the non-significant linear relationship between  $\text{NH}_4^+$ -N deposition and distance from the urban core (Fig. 2b).  $\text{NO}_x$  can be transported over long distance from its sources because of its long lifetime and transportation capacity (Sharma et al. 2011; Gao et al. 2012). So it was not surprised that the deposition of  $\text{NO}_3^-$ -N is correlated with distance from the urban core (Fig. 2a).

The importance of distance in influencing the transport and deposition of pollutants was also recognized by Fowler et al. (2007). According to emission-deposition patterns, the changes of emission and deposition in the source regions are close to linear while non-linearity is larger for the receptor regions as in those regions, local emissions are often limited and the deposition is very sensitive to changes in emission upwind. Based on the linear relationship between wet inorganic N deposition and distance from the urban core (Fig. 2), the PRD region could be considered as a source region in which N deposition is dominantly influenced by the local emission,

**Table 2** Correlation coefficients between N deposition with N contents and  $\delta^{15}\text{N}$  value in moss

	Inorganic N deposition	$\text{NH}_4^+$ -N deposition	$\text{NO}_3^-$ -N deposition	Moss $\delta^{15}\text{N}$
$\text{NH}_4^+$ -N deposition	0.925**			
$\text{NO}_3^-$ -N deposition	0.903**	0.711**		
Moss $\delta^{15}\text{N}$	-0.551*	-0.370	-0.632*	
Ratios of $\text{NH}_4^+$ -N deposition to $\text{NO}_3^-$ -N deposition	0.660**	0.873**	0.300	-0.102

\*Correlation is significant at the 0.05 level (two-tailed)

\*\*Correlation is significant at the 0.01 level (two-tailed)

rather than the long-range transport from outside. The anthropogenic N emission in this region can be inferred by a list of sources in the following paragraph. As a source region, the PRD region greatly impacts the levels of inorganic N deposition in this region and further beyond.

The main sources of wet inorganic N deposition

In the PRD region, agricultural source is the largest contributor to  $\text{NH}_3$  emissions accounting for about 85.4 % of the total anthropogenic  $\text{NH}_3$  emissions, followed by sewage treatment and on-road mobility with 3.3 and 2.5 %, respectively (Zheng et al. 2012). For  $\text{NO}_x$  emissions, about 41.3 % came from power plants, 45.9 % from mobile sources, and 12.8 % from others (Zheng et al. 2009). Both  $\text{NH}_3$  and  $\text{NO}_x$  emissions are largely related to urbanization activities shown by the significant correlation ( $R^2=0.711$ ,  $P<0.01$ ) between  $\text{NH}_4^+-\text{N}$  deposition and  $\text{NO}_3^--\text{N}$  deposition. In this study, the ratios of  $\text{NH}_4^+-\text{N}/\text{NO}_3^--\text{N}$  larger than 1 (see Fig. 2d), showed that  $\text{NO}_x$  emission from fossil fuel combustion during transport, industry, and energy production has more important impacts on inorganic N deposition compared to  $\text{NH}_3$  emission. Therefore, it is vital to identify  $\text{NO}_x$  sources for developing sound regulatory management and mitigation strategies to control N pollution (Elliott et al. 2007, 2009).

Moss  $\delta^{15}\text{N}$  value is a good bio-indicator of different N sources (Liu et al. 2008; Xiao et al. 2010). Less negative  $\delta^{15}\text{N}$  values can be linked to emissions of oxidized N (Pearson et al. 2000). Relatively, higher  $\delta^{15}\text{N}$  values of mosses sampled in the most polluted and acidified areas seem to be related to the higher contribution of  $\text{NO}_x$  emitted by industrial activities, primarily fossil fuel combustion (Bragazza et al. 2005). The moss  $\delta^{15}\text{N}$  values in urban areas are higher than those in rural areas, suggesting that rural mosses are influenced more by the reduced form of N ( $\text{NH}_4^+-\text{N}$ ) than by the oxidized N species ( $\text{NO}_3^--\text{N}$ ) (Xiao and Liu 2002; 2004). In this study, a significantly negative correlation was found between  $\delta^{15}\text{N}$  values of moss and  $\text{NO}_3^--\text{N}$  deposition ( $R^2=-0.632$ ,  $P<0.05$ ) (Table 2), showing that regional  $\delta^{15}\text{N}$  variability correlates with  $\text{NO}_x$  emission (Elliott et al. 2007). In addition, the significant positive correlation between distance from the urban core and  $\delta^{15}\text{N}$  values in moss also indicated that  $\text{NO}_x$  contribution to wet inorganic N deposition gradually decreased with the distance (Fig. 4).

In this study, moss  $\delta^{15}\text{N}$  values were in the range of 0 to  $-6$  ‰. According to the  $\delta^{15}\text{N}$  inventories of potential sources of N in the atmosphere (Heaton 1986, 1990; Chen et al. 2011), we concluded that the main anthropogenic sources of wet inorganic N deposition in PRD originate mostly from transportation emission as reported by Zheng et al. (2009) and Huang et al. (2013). The numbers of automotive vehicles exceeded  $9.1 \times 10^6$  in 2011 in Guangdong Province (Shen 2013) which supports our conclusion. Negative  $\delta^{15}\text{N}$ -value

was evident in wet deposition at Guangzhou (Jia and Chen 2010). Comparing with moss  $\delta^{15}\text{N}$ -value ( $-1.82 \pm 3.44$  ‰) in the Yangtze River drainage basin (Xiao et al. 2010), moss  $\delta^{15}\text{N}$ -value in our study was more negative, which were comparable to that ( $-3.05$  to  $-7.48$  ‰) of wet deposition in Xiamen Bay area, China (Chen et al. 2011). Therein, controlling  $\text{NO}_x$  emission should be an important target of the region.

## Conclusions

Urbanization increases the contribution of  $\text{NO}_3^--\text{N}$  to wet inorganic N deposition by increasing  $\text{NO}_x$  emission. In turn,  $\text{NO}_x$  becomes the more important source of N deposition compared to  $\text{NH}_3$ , which is mainly from the emission from transportation. Distance from the urban core could be considered as a useful indicator of the levels of wet inorganic N deposition in the urbanized regions as indicated by its significant linear relationship with N deposition. Controlling  $\text{NO}_x$  emission especially the emission of vehicles should be an effective measurement to reduce N deposition in China.

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