**Atmospheric
Chemistry
and Physics**

Anthropogenic imprints on nitrogen and oxygen isotopic composition of precipitation nitrate in a nitrogen-polluted city in southern China

Y. T. Fang[1,2], K. Koba[2], X. M. Wang[3], D. Z. Wen[1], J. Li[1], Y. Takebayashi[2], X. Y. Liu[2], and M. Yoh[2]

[1]South China Botanical Garden, Chinese Academy of Sciences, Guangzhou 510650, China
[2]Tokyo University of Agriculture and Technology, Tokyo 183 8509, Japan
[3]School of Environmental Science and Engineering, Sun Yat-Sen University, Guangzhou 501275, China

Abstract. Nitric acid (HNO_3) or nitrate (NO_3^-) is the dominant sink for reactive nitrogen oxides ($NO_x = NO + NO_2$) in the atmosphere. In many Chinese cities, HNO_3 is becoming a significant contributor to acid deposition. In the present study, we measured nitrogen (N) and oxygen (O) isotopic composition of NO_3^- in 113 precipitation samples collected from Guangzhou City in southern China over a two-year period (2008 and 2009). We attempted to better understand the spatial and seasonal variability of atmospheric NO_x sources and the NO_3^- formation pathways in this N-polluted city in the Pearl River Delta region. The $\delta^{15}N$ values of NO_3^- (versus air N_2) ranged from -4.9 to $+10.1‰$, and averaged $+3.9‰$ in 2008 and $+3.3‰$ in 2009. Positive $\delta^{15}N$ values were observed throughout the year, indicating the anthropogenic contribution of NO_x emissions, particularly from coal combustion. Different seasonal patterns of $\delta^{15}N$-NO_3^- were observed between 2008 and 2009, which might reflect different human activities associated with the global financial crisis and the intensive preparations for the 16th Asian Games. Nitrate $\delta^{18}O$ values (versus Vienna Standard Mean Ocean Water) varied from $+33.4$ to $+86.5‰$ (average $+65.0‰$ and $+67.0‰$ in 2008 and 2009, respectively), a range being lower than those reported for high latitude and polar areas. Sixteen percent of $\delta^{18}O$ values was observed lower than the expected minimum of $+55‰$ at our study site. This was likely caused by the reaction of NO with peroxy radicals; peroxy radicals can compete with O_3 to convert NO to NO_2, thereby donate O atoms with much lower $\delta^{18}O$ value than that of O_3 to atmospheric NO_3^-. Our results highlight that the influence of human activities on atmospheric chemistry can be recorded by the N and O isotopic composition of atmospheric NO_3^- in a N-polluted city.

1 Introduction

Global atmospheric emissions of nitrogen oxides (NO_x, the sum of NO and NO_2) have increased dramatically during the past 150 years (Galloway et al., 2004, 2008). Current global NO_x emissions are dominated by fossil fuel combustion (63%) and far exceed natural NO_x sources, such as lightning, biogenic soil processes, and wildfires (Ehhalt et al., 2001). NO_x contributes to the formation of ozone (O_3) and particulate matter and is thus an important factor affecting regional air quality and radiative balance (Ehhalt et al., 2001). Once emitted to the atmosphere, NO_x is oxidized via several pathways to form highly soluble nitric acid (HNO_3), which is then dissolved in precipitation or collected on aerosols and subsequently scavenged from the atmosphere as wet or dry deposition (Ehhalt et al., 2001; Elliott et al., 2009). The elevated atmospheric deposition of NO_3^- associated with increased NO_x emissions also poses many ecological and environmental threats, including the acidification of soil and surface water, the eutrophication of lakes, rivers, and estuaries, the loss of biodiversity, and the alteration of global carbon budget (Vitousek et al., 1997; Aber et al., 1998; Gundersen et al., 1998; Fang et al., 2008; Galloway et al., 2008).
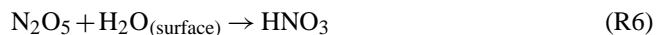
The growth rate in NO_x emissions is expected to have shifted from North America and Europe to Asia (Ehhalt et al., 2001). In China, HNO_3 is becoming a significant contributor

to acid rain due to the increased vehicle usage and power plant emissions (Zheng et al., 2009; Wang et al., 2010), and to the control on SO_2 emissions (Zhao et al., 2009) in many cities. For example, in Guangzhou City in southern China, the molar ratios of sulfate (SO_4^{2-}) to NO_3^- in precipitation have decreased continuously from 4.6 in 1986–1990 to 2.8 in the 1990s and to 1.5 in the 2000s (Fig. 1). Thus, it is important to recognize and separate the anthropogenic production of NO_x (and therefore NO_3^-) from natural processes (e.g., soil emissions, biomass burning, and lightning) in order to assess the impact of anthropogenic input on the atmospheric cycle and the budget of reactive N (Ehhalt et al., 2001). The identification of NO_x sources at any given location is also vital to develop sound regulatory management and mitigation strategies for air and water quality (Elliott et al., 2007, 2009).

Once released to the atmosphere, NO_x is converted to atmospheric NO_3^- through a number of chemical pathways (Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts, 2000). Most tropospheric NO_x is emitted as NO, which photochemically equilibrates during the daytime with NO_2 within a few minutes (Reactions R1 and R2); this NO_2 is further oxidized via several major chemical reaction pathways. During the day, the photolytic production of hydroxyl (OH) radical results in the oxidation of NO_2 to HNO_3(g) via the OH radical (Reaction R3). This pathway is also most prevalent in summer when the concentrations of photochemically produced OH radicals are the highest (Calvert et al., 1985); this is termed the OH pathway hereafter. At nighttime, NO_2 is oxidized by O_3 to produce NO_3 radical (NO_3) (reaction R4), which subsequently combines with NO_2 to form dinitrogen pentoxide (N_2O_5) (Reaction R5). The hydrolysis of N_2O_5 yields HNO_3(g) (Reaction R6). This pathway is most prevalent during winter as N_2O_5 is thermally unstable (Calvert et al., 1985), and is termed the N_2O_5 pathway hereafter.

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (R1)$$

$$NO_2 + h\upsilon \rightarrow NO + O \qquad (R2)$$

$$NO_2 + OH \rightarrow HNO_3 \qquad (R3)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (R4)$$

$$NO_3 + NO_2 \leftrightarrow N_2O_5 \qquad (R5)$$

$$N_2O_5 + H_2O_{(surface)} \rightarrow HNO_3 \qquad (R6)$$

The N stable isotopic composition of atmospheric deposition has often been viewed as reflecting NO_x source because N atoms are conserved during the transformation of NO_x into NO_3^- in the atmosphere (Moore, 1977; Freyer, 1991; Heaton, 1990; Hastings et al., 2003), although N isotopic fractionation may also occur during atmospheric transformations and during the transport of atmospheric NO_3^-. The $\delta^{15}N$ values of anthropogenic and natural NO_x sources vary over a large range. The NO_x emitted by anthropogenic sources can
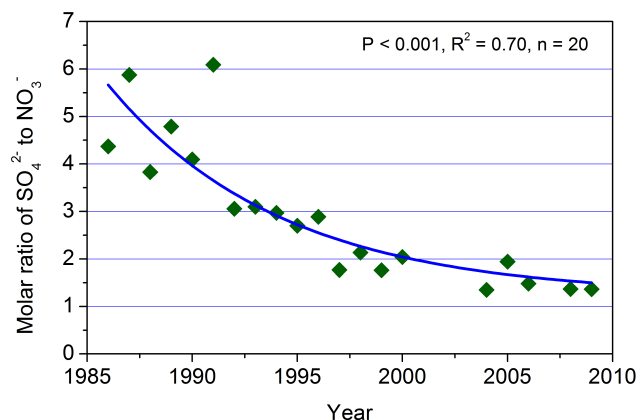

Fig. 1. Molar ratios of SO_4^{2-} to NO_3^- in precipitation in Guangzhou City during the period from 1986 to 2009. Data are from Quan et al. (1992) for 1986 to 1990, Ye et al. (2008) for 1991 to 2000, Liu et al. (2006) for 2004, Huang et al. (2009) for 2005, Cao et al. (2009) for 2006, and this study for 2008 and 2009.

be classified into two groups, fuel NO_x (i.e., the oxidation of N initially contained in the fuel) and thermal NO_x (i.e., high-temperature conversion of atmospheric N_2 and O_2 to NO_x) (Snape et al., 2003; Widory, 2007). The fuel NO_x generally shows positive values. For instance, the $\delta^{15}N$ of NO_x from coal-fired power plants range from +5 to +13‰ (Heaton, 1990; Kiga et al., 2000) and was determined on the order of +15 ± 2‰ (Snape et al., 2003). In contrast, the $\delta^{15}N$ of thermal NO_x exhibits negative values. Heaton (1990) reported the $\delta^{15}N$ values of NO_x for vehicle exhaust of −13 to −2‰ under different loads. Snape et al. (2003) measured values on the order of −6.2 ±0.9 from the exhaust of an industrial plant. The $\delta^{15}N$ of vehicular NO_x are determined by the relative proportion of thermal and fuel NO_x produced in car and truck engines. The NO_x emissions measured from tailpipe exhaust, roadside denuders, and roadside vegetation have $\delta^{15}N$ values of +3.7, +5.7, and +3.8‰, respectively (Moore, 1977; Ammann et al., 1999; Pearson et al., 2000). The $\delta^{15}N$ values of natural NO_x sources, including lightning, biogenic NO_x emissions, and biomass burning, have not yet been well quantified. Hoering (1957) reported that the $\delta^{15}N$ values of NO_x produced during electrical discharge used to simulate lightning range from −0.5 to +1.4‰. The $\delta^{15}N$ values are −48 to −20‰ for NO emitted by fertilized soil (Li and Wang, 2008). Low $\delta^{15}N$ values were found at pristine sites relative to polluted sites (Moore, 1977; Pearson et al., 2000), and during spring and summer relative to other seasons (Freyer, 1991; Russell et al., 1998).

Oxygen isotopic fractionation can induce large variations in $\delta^{18}O$ values between the reactants and the products during atmospheric transformation (see e.g., Chakraborty and Chakraborty, 2003), but $\delta^{18}O$ of atmospheric NO_3^- is considered to be mostly related to oxidation pathways in the atmosphere, involving such atmospheric oxidants as O_3, OH

radicals, peroxy radicals, and halogen oxides (Hastings et al., 2003, 2004; Michalski et al., 2003; Morin et al., 2008, 2009; Alexander et al., 2009). The oxidation reactions are influenced by many factors, including temperature, humidity, solar radiation, and the availability of reactive aerosol surfaces (Wankel et al., 2010). The $\delta^{18}O$ values of atmospheric NO_3^- are mostly controlled by the seasonality of the chemical oxidation pathways (Reactions R1–R6) due to the high $\delta^{18}O$ values contributed by tropospheric O_3 (+90 to +120‰, Krankowsky et al., 1995; Johnston and Thiemens, 1997) during NO_3^- formation (Hastings et al., 2003; Michalski et al., 2003). The O isotopic composition of HNO_3 formed by the OH pathway reflects the contribution of up to 2/3 O_3 and 1/3 OH, whereas the O isotopic composition of HNO_3 formed by the N_2O_5 pathway reflects the contribution of up to 5/6 O_3 and 1/6 H_2O (Hastings et al., 2003). Thus, atmospheric NO_3^- formed via the OH pathway has lower $\delta^{18}O$ values than that formed via the N_2O_5 pathway. The N_2O_5 pathway is more important in winter than in summer due to the longer nighttime in the former. This explains the higher $\delta^{18}O$ of atmospheric NO_3^- in winter than in summer in previous studies (Hastings et al., 2003, 2004; Elliott et al., 2007, 2009; Morin et al., 2008, 2009; Wankel et al., 2010).

The dual isotopes of atmospheric NO_3^- have been intensively analyzed in middle and high latitude regions in an effort to constrain NO_x sources and formation pathways (Hastings et al., 2003; Elliott et al., 2007, 2009; Morin et al., 2008, 2009). For instance, Elliott et al. (2007, 2009) demonstrated a strong correlation between wet deposition $\delta^{15}N$-NO_3^- and proximity of stationary source (e.g., power plant facilities) NO_x emissions in the northeastern US, with higher $\delta^{15}N$ values (up to +3.2‰) found in areas affected by higher NO_x emissions, suggesting that the nitrate isotope is a promising tool to constrain NO_x sources to a given location. To date, little work has been done to characterize the dual isotopic composition of atmospheric N deposition in low latitude regions (Morin et al., 2009; Wankel et al., 2010), particularly in a location with complex air pollution under warm and humid conditions, such as the city we studied.

In this study, we measured the N and O isotopic composition of NO_3^- in 113 precipitation samples collected from Guangzhou City in southern China over a two-year period (2008 and 2009). Guangzhou City is located in the center of the Pearl River Delta. It is highly populated and is one of the major economic centers in China. In the last three decades, rapid economic development has led to complex and regional air pollution problems, such as acid rain, photochemical smog, and haze, over this region (Wang et al., 2003, 2007, 2010; Zhang et al., 2008a; Zheng et al., 2009). We attempted to better understand the spatial and seasonal variability of atmospheric NO_x sources in this N-polluted city and the NO_3^- formation pathways in combination with air mass back trajectory analysis, which would help us evaluate the impact of urban development and industrialization on the N input to the study region.

Our hypotheses were that in the study city, (1) there would be a distinct seasonal pattern of $\delta^{15}N$-NO_3^- in precipitation with lower values in the warm season due to a higher contribution from biogenic sources (e.g., soil emissions) and the prevailing southern winds from South China Sea, which bring relatively clean air masses to the study city, than in the cool season; (2) due to anthropogenic N emissions, $\delta^{15}N$-NO_3^- values would be higher than those of other remote areas; (3) $\delta^{18}O$-NO_3^- would be lower in the warm season than in the cool season due to the longer daytime in the warm season, as previously reported (Hastings et al., 2003, 2007; Elliott et al., 2009), but the seasonal variation would be small compared to those of high latitude and polar areas; and (4) $\delta^{18}O$-NO_3^- would be lower than those of high latitude and polar areas due to the relative longer daytime and the more abundant water vapor, as our study site is close to the equator (humid tropical climate). However, we also expected that the seasonal N and O isotopic patterns might have been affected by the energy consumption pattern associated with certain events, such as the global financial crisis in 2008 and the intensive construction activities preparing for the 16th Asian Games in 2009.

2 Methods

2.1 Sampling

From 2008 to 2009, bulk precipitation was collected in the South China Botanical Garden (23.2° N, 113.3° E) of Guangzhou City on a daily basis. In some months, no precipitation could be sampled owing to the small volume and the prolonged drought, which resulted in an underestimation of the annual precipitation N input. Precipitation was collected with an open funnel (23 cm in diameter) that was connected to a 5 L sampling bottle with a black polypropylene tube. The collector was washed with distilled water immediately after each collection. Samples were filtered within 24 h of collection through 0.45 μm filters in the laboratory, and then stored in plastic bottles at 4 °C until chemical analysis.

2.2 Chemical and isotope analyses

The concentrations of major ions, including NH_4^+, NO_2^-, and NO_3^-, in all precipitation samples were determined by ion chromatography (Dionex DX-120, Osaka, Japan). The $\delta^{15}N$ (versus air N_2) and $\delta^{18}O$ (versus Vienna Standard Mean Ocean Water) values of NO_3^- in precipitation were measured using the denitrifier method (Sigman et al., 2001; Casciotti et al., 2002), with an isotope-ratio mass spectrometer (Delta XP; Thermo Fisher Scientific K.K., Yokohama, Japan) coupled with a gas chromatograph (HP6890; Hewlett Packard Co., Palo Alto, CA, USA) equipped with a PoraPLOT column (25 m × 0.32 mm) and GC interface III (Thermo Fisher Scientific K. K., Yokohama, Japan).

The denitrifying bacterium, *Pseudomonas aureofaciens*, was used to convert 25 nmol of NO_3^- into gaseous N_2O in 20 mL vials prior to isotope analysis. We ran several standards (USGS32, 34, and 35, and IAEA NO_3^-) to obtain the calibration curve to correct for drift, oxygen isotope exchange, and blank. The average standard deviations for replicate analysis of an individual sample were ± 0.2‰ for $\delta^{15}N$ of NO_3^- and ± 0.5‰ for $\delta^{18}O$.

Atmospheric NO_3^- is anomalously enriched in both the $^{18}O/^{16}O$ and $^{17}O/^{16}O$ isotopic ratios, due to the transfer from O_3 to HNO_3 during NO_x oxidation reactions (Michalski et al., 2003). The use of the denitrifier method for $\delta^{15}N$ measurements thus requires correction for the contribution of the mass-independent ^{14}N-^{14}N-^{17}O (the m/z 45 signal) to the analyte N_2O (see Hastings et al., 2003, 2004). In this paper, we report the uncorrected results; the mass independence of ^{17}O relative to the m/z 45 signal of N_2O generated from NO_3^- deposition was reported to result in a mean lowering of the $\delta^{15}N$ values by approximately -1.5‰ (Elliott et al., 2009; Wankel et al., 2010). As denitrifying bacteria convert both NO_3^- and NO_2^- to N_2O, the $\delta^{15}N$ values reported here represent the combined pools of NO_2^- and NO_3^-. The presence of NO_2^- interferes with the analyses of $\delta^{18}O$-NO_3^- and may result in some errors (Casciotti et al., 2002; Casciotti et al., 2007). In a similar study of the dual isotopes of aerosol NO_3^-, Wankel et al. (2010) found average corrections for NO_2^- interferences to be $+3.3$‰ for samples in which NO_2^- concentrations were 3% of total NO_3^- plus NO_2^-. In our study, four rainwater samples contained more than $5 \, \mu mol \, L^{-1} \, NO_2^-$, but NO_2^- made up on average 1.6% of total NO_3^- plus NO_2^- for all the samples over the study period. Assuming that $\delta^{18}O$ of NO_2^- is the same as $\delta^{18}O$ of water (-15 to $+0$‰), NO_2^- contributes 1.6% to $(NO_2^- + NO_3^-)$ and we can apply the calibration curve for NO_2^- with denitrifier reported by Casciotti et al. (2007), the NO_2^- will drop the values of $\delta^{18}O$-NO_3^- by 1.1–1.3‰. Thus, it was a minor analytical artifact resulting from the presence of NO_2^- in this study.

2.3 Backward trajectories

To analyze the impact of air mass transportation, 72-hour backward trajectories were computed for all sample days using NOAA's Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) (http://ready.arl.noaa.gov/HYSPLIT_traj.php) (Draxler and Rolph, 2010) at an altitude of 500 m a.g.l. In this case, terrain height, ambient temperature, rainfall and relative humidity were used with HYSPLIT to calculate the back trajectories. The time frame was chosen since the lifetime of NO_x in the boundary layer is generally less than 2 days, with a longer lifetime expected in the winter than in the summer, and since HNO_3 generally has a similar atmospheric lifetime of 1–2 days (Liang et al., 1998). The air mass sectors were categorized to be of continental origin (i.e., the mainland of China) or marine origin

(e.g., from the South China Sea or the Philippine Sea), according to the starting point of air mass transportation (72 hours before arrival at Guangzhou). The air masses starting over southern Asian countries like Thailand and Vietnam were considered to be of marine origin in this study because they passed through the South China Sea.

2.4 Calculations and statistical analysis

Annual N load from precipitation is the sum of the product of concentration and water amount for each sampling period. In this paper, both arithmetic and volume-weighted means were presented for NO_3^- concentration. For isotopic composition, in addition to arithmetic mean, NO_3^--flux-weighted mean was also presented because isotopic composition was determined not only by volume but also by concentration. One-way ANOVA was performed for concentration, $\delta^{15}N$, and $\delta^{18}O$ of precipitation NO_3^- in order to identify the differences between seasons and between air mass sources for each year. Two-way ANOVA was used to identify the significance between years, seasons, and air mass sources for the investigated variables across the study period. Correlation analysis with the two-tail significance test was used to examine the relationships between variables across the study period or in the individual year. All analyses were conducted using PASW Statistics 18.0 for Windows. Statistically significant differences were set at P values <0.05 unless otherwise stated.

3 Results

3.1 Precipitation NO_3^- input

For the 113 precipitation samples collected in Guangzhou City, NO_3^- concentration ranged from 6 to $256 \, \mu mol \, L^{-1}$, except for one rain event on 17 September 2008 that had an unusually high concentration ($406 \, \mu mol \, L^{-1}$) (Fig. 2b). As the isotope results for this sample were not anomalous (Fig. 2c, d), we considered that there was no contamination and the data were included in the data analysis. Two-way ANOVA using year and season as main factors showed that NO_3^- concentration was not significantly different between years (Table 1). Mean NO_3^- concentration was higher during the cool season (October to March) than during the warm season (April to September) in 2008, but the reverse was true in 2009 (Table 2).

The amounts of precipitation were 2162 mm in 2008 and 1931 mm in 2009, with 77% and 79% falling during the warm season (Fig. 2a, Table 2). The annual NO_3^- input in precipitation was 16.0 and 18.5 kg N ha^{-1} in the two study years, with 74% and 80% falling in the warm season (Table 2). Continental precipitation accounted for 38% and 31% of the annual precipitation amount in 2008 and 2009,

Table 1. Ranges and means of concentration, δ^{15}N, and δ^{18}O of NO_3^- in precipitation.

| | | NO_3^- con. (μmol L^{-1}) | | | δ^{15}N-NO_3^- (‰) | | | | δ^{18}O-NO_3^- (‰) | | |
	Range	Mean[a]	Mean[b]	Range	Mean[a]	Mean[b]	Mean[c]	Range	Mean[a]	Mean[b]	Mean[c]
2008	6 to 406	63	53	−3.9 to +7.9	+3.9	+3.7	+4.2	+33.4 to +81.5	+65.0	+64.9	+71.8
2009	9 to 256	77	68	−4.9 to +10.1	+3.3	+3.0	+3.5	+48.2 to +86.2	+67.7	+66.5	+70.6

[a] arithmetic mean.
[b] volume-weighted mean.
[c] NO_3^--flux-weighted mean.

Table 2. Seasonal comparison of concentration, δ^{15}N, and δ^{18}O of NO_3^- in precipitation.

Year	Season	n	Precipitation (mm)	NO_3^- input (kg N ha^{-1} a^{-1})	NO_3^- con. (μmol L^{-1})	δ^{15}N-NO_3^- (‰)	δ^{18}O-NO_3^- (‰)
2008	Cool	9	491	4.1	89.9 (9 to 181, 19.6)	+4.5 (+0.3 to +7.5, 0.7)	+73.2 (+53.3 to +81.2, 3.2)
	Warm	50	1670	11.9	57.7 (6 to 406, 9.4)	+3.8 (−3.9 to +7.9, 0.3)	+63.5 (+33.4 to +81.5, 1.4)
	P value				0.18	0.41	0.01
2009	Cool	11	411	3.7	67.6 (19 to 181, 14.5)	+0.7 (−4.9 to +4.3, 0.9)	+73.0 (+59.3 to +84.4, 2.7)
	Warm	43	1520	14.8	78.8 (10 to 256, 9.1)	+4.1 (+0.5 to +10.1, 0.3)	+66.4 (+47.2 to +86.2, 1.5)
	P value				0.57	<0.001	0.05

The P values were obtained by one-way ANOVA performed for each study year. Range (minimum and maximum) and one standard error of mean are given in parentheses.
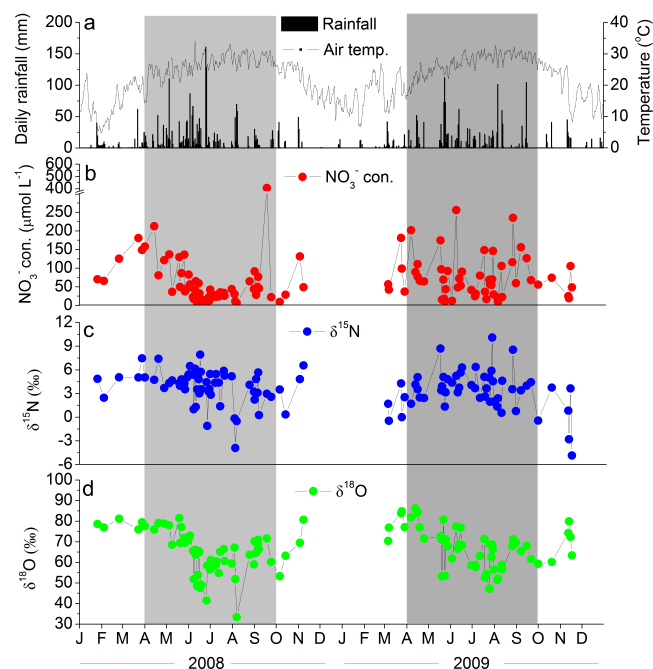

Fig. 2. Daily precipitation and mean air temperature (**a**), NO_3^- concentration (**b**), δ^{15}N-NO_3^- (**c**), and δ^{18}O-NO_3^- (**d**) in precipitation from 2008 through 2009 in Guangzhou City. The shaded areas denote the warm seasons from April to September.

respectively (Fig. 3), but brought proportionally more NO_3^- input (52% and 41% of annual NO_3^- input) due to the higher NO_3^- concentration (Table 3).

3.2 N isotopes of NO_3^-

Our measurements of δ^{15}N of precipitation NO_3^- over the study period varied between −4.9‰ and +10.1‰, with annual mean values of +3.9‰ in 2008 and +3.3‰ in 2009, respectively (Fig. 2c, Table 1). Positive δ^{15}N values were observed throughout 2008, but some negative values or near zero values were observed in the summer (Fig. 2c). However, the seasonal difference between the warm and cool seasons was not significant in that year (Table 2). There was also no significant difference in δ^{15}N values between continental and marine sources (Table 3). In 2009, δ^{15}N of NO_3^- in the warm season was significantly higher than that in the cool season (Table 2).

3.3 O isotopes of NO_3^-

The δ^{18}O values of NO_3^- ranged from +33.4 to +86.2‰ (Fig. 2d), with annual mean values of +65.0‰ and +67.7‰ in 2008 and 2009, respectively (Table 1). The NO_3^--flux-weighted δ^{15}N values were +71.8‰ in 2008 and +70.6‰ in 2009 (Table 1). The seasonal pattern of δ^{18}O of NO_3^- was clear, with values reaching a minimum in July or August. As a result, the δ^{18}O values of NO_3^- were significantly higher in the cool season than in the warm season for both study years

Table 3. Sources comparison of concentration, δ^{15}N, and δ^{18}O of NO_3^- in precipitation.

Year	Season	n	Precipitation (mm)	NO_3^- input (kg N ha^{-1} a^{-1})	NO_3^- con. (μmol L^{-1})	δ^{15}N-NO_3^- (‰)	δ^{18}O-NO_3^- (‰)
2008	Continental	21	824	8.4	95.2 (9 to 406, 19.0)	+3.4 (−3.9 to +7.4, 0.6)	+71.6 (+51.8 to +81.5, 1.9)
	Marine	38	1337	7.6	44.5 (6 to 212, 6.9)	+4.2 (−1.1 to +7.9, 0.3)	+61.3 (+33.4 to +79.5, 1.6)
	P value				0.004	0.22	<0.001
2009	Continental	19	589	8.3	83.1 (12 to 202, 13.0)	+1.9 (−4.9 to +8.7, 0.7)	+71.6 (+58.8 to +84.8, 1.9)
	Marine	35	1342	12.1	73.0 (10 to 256, 9.8)	+4.1 (+1.1 to +10.1, 0.3)	+65.5 (+47.2 to +86.2, 1.7)
	P value				0.53	0.002	0.06

The P values were obtained by one-way ANOVA performed for each study year. Range (minimum and maximum) and one standard error of mean are given in parentheses.
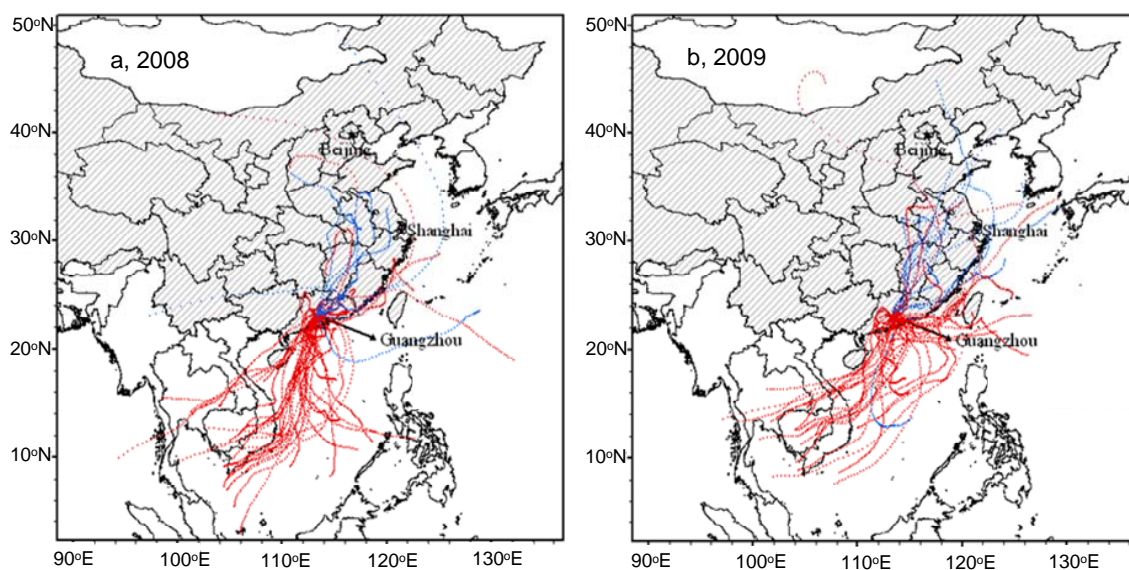

Fig. 3. 72-hour air mass backward trajectories for all sampling days in Guangzhou City, based on NOAA HYSPLIT model back trajectories. Lines in blue denote air mass trajectories occurring in the cool season and those in red denote trajectories in the warm season.

(Fig. 2d, Table 2). The continental source precipitation had higher δ^{18}O of NO_3^- than the marine source precipitation; the continental source precipitation mainly occurred in the cool season that had shorter daytime (Fig. 3).

4   Discussion

4.1   Nitrogen deposition

At our study site, NH_4^+ contributed an additional 14.9 kg N ha^{-1} a^{-1} in 2008 and 21.8 kg N ha^{-1} a^{-1} in 2009 to N deposition in precipitation, respectively (data not shown). Thus, the total inorganic N input was 30.9 and 40.3 kg N ha^{-1} a^{-1} in 2008 and 2009, respectively. Compared with the small measured N deposition of 1.8–3.2 kg N ha^{-1} a^{-1} in some remote areas in China (Liu et al., 1993) and of 0.9 kg N ha^{-1} a^{-1} in Hawaii (Carrillo et al., 2002), we suggest that such high bulk N deposition at the study site can be an important N input to terrestrial and

aquatic ecosystems therein and that elevated N deposition is mainly caused by increased human activities associated with industrialization and urbanization.

4.2   Seasonal pattern of N isotopes of NO_3^-

Our measurements of δ^{15}N of precipitation NO_3^- over the study period varied between −4.9‰ and +10.1‰, with a total arithmetic mean of +3.6‰ (Fig. 2, Table 1). These observed values fall well within the wide range of previously reported values for atmospheric NO_3^- (Russell et al., 1998; Hastings et al., 2003; Heaton et al., 2004; Elliott et al., 2007, 2009; Kendall et al., 2007; Savarino et al., 2007; Morin et al., 2009) and are comparable to the results for urban or suburban sites in China (Zhang et al., 2008b; also see Supplement). Our results are higher than those in precipitation or particulate NO_3^- in two rural sites in Hebei in northern China, most sites in Japan, over the Atlantic Ocean and the Pacific Ocean, and in the polar regions (Supplement), where most values are negative. Our measured values of δ^{15}N of precipitation NO_3^-

were generally higher than the reports for wet deposition in the US (Elliott et al., 2007, 2009; Goodale et al., 2009 and references therein). For example, across 33 sites in the midwestern and northeastern US, $\delta^{15}N$ of wet NO_3^- deposition ranged from -8.1 to $+3.2‰$, with a mean of $-1.5‰$ (Elliott et al., 2007, Supplement). A wider range of $\delta^{15}N$ of atmospheric NO_3^- was observed in Europe (Freyer, 1978, 1991; Yeatman et al., 2001; Widory, 2007, and Supplement). Cautions may be needed when comparing $\delta^{15}N$ data from different atmospheric matrices, because the $\delta^{15}N$ of aerosol NO_3^- is very different from that of rainwater NO_3^- in some studies (e.g., aerosol nitrate $\delta^{15}N$ was 9‰ higher than rainwater nitrate $\delta^{15}N$ in Jülich, a moderately polluted city of German; Freyer, 1991, Supplement) while is not in other studies (Baker et al., 2007; or see Morin et al., 2009).

Seasonality has been commonly reported for isotopic composition of atmospheric NO_3^- (Hastings et al., 2003; Elliott et al., 2007, 2009; Morin et al., 2008; Wankel et al., 2010). The seasonal pattern of $\delta^{15}N$ seems to vary from site to site. In a study performed in the Arctic, temperature was found to be a major determinant of $\delta^{15}N-NO_3^-$ values in all seasons except spring when snowpack emissions are maximal (Morin et al., 2008). Temperature was also found to significantly influence $\delta^{15}N-NO_3^-$ in both dry and wet depositions across the region of Ohio, New York, and Pennsylvania in the US, with lower values in summer months than in winter months (Elliott et al., 2009). By contrast, in Bermuda in the North Atlantic Ocean (Hastings et al., 2003) and in Eilat, Israel (Wankel et al., 2010), $\delta^{15}N$ of atmospheric NO_3^- was significantly higher in the warmer season. The difference in pattern is likely to be a result of the shift in NO_x sources for those studies. In the present study, $\delta^{15}N-NO_3^-$ was correlated with temperature only in 2009 (Fig. 4b). The high $\delta^{15}N-NO_3^-$ values in coincidence with the high temperatures observed in 2009 (Table 2) might be caused by the high demand for fossil fuel because of the intense preparations for the 16th Asian Games (see below).

In the present study, we initially expected that the precipitation with a marine origin would have similar $\delta^{15}N$ values of NO_3^- to those reported for the atmospheric matrices collected above oceans. The $\delta^{15}N$ values of atmospheric NO_3^- were -7.1 to $-1.6‰$ (average $-4‰$) in the low latitude regions of the Atlantic Ocean (between 45° S and 45° N) (Morin et al., 2009). Baker et al. (2007) reported that $\delta^{15}N$ of atmospheric NO_3^- from those areas ranged from -11 to $+2.8‰$ and averaged $-3‰$. A similar range (-14 to $+1.8‰$, average $-2.1‰$ in the warm season and $-5.9‰$ in the cool season) was observed for $\delta^{15}N$ of rain NO_3^- in Bermuda in the North Atlantic Ocean (Hastings et al., 2003). The $\delta^{15}N$ values of precipitation NO_3^- in two Hawaiian islands in the Pacific Ocean were reported to range narrowly from -3.8 to $+2.4‰$ (average, $-0.03‰$ and $-2.9‰$, respectively) (Carrillo et al., 2002). We did observe a few negative values as previously reported during storms in the summer of 2008, but
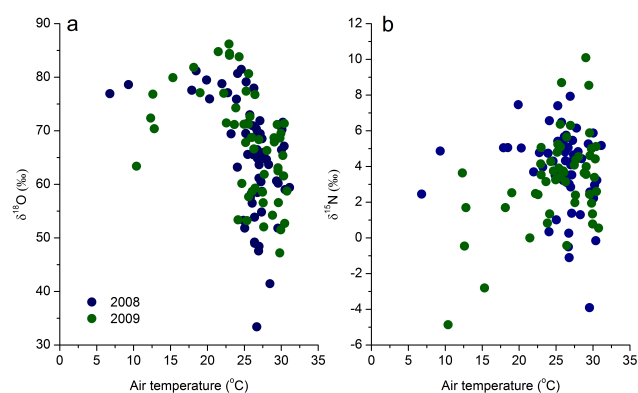

Fig. 4. $\delta^{18}O-NO_3^-$ **(a)** and $\delta^{15}N-NO_3^-$ **(b)** vs. mean air temperature three days prior to sampling over the study period. For panel **(a)**, $R^2 = -0.21$, $P < 0.001$ in 2008; and $R^2 = -0.20$, $P = 0.001$ in 2009. For panel **(b)**, $R^2 = -0.03$, $P = 0.222$ in 2008; and $R^2 = 0.24$, $P < 0.001$ in 2009.

most values were positive during the study period (Fig. 2c). Furthermore, we found that the averaged $\delta^{15}N$ values were lower for precipitation from the continent than for that from the sea, particularly in 2009 (Table 3). Over the two study years, $\delta^{15}N$ was $+4.1‰$ in precipitation from the sea, and was significantly ($P = 0.017$) higher than $+3.1‰$ from the continent. The mean NO_3^- concentration in the marine source precipitation (on average 44 and 73 $\mu mol\,L^{-1}$ in 2008 and 2009, respectively, Table 3) was far higher than the annual means (0.5 to 2 $\mu mol\,L^{-1}$) in Hawaii (Carrillo et al., 2002). The high $\delta^{15}N$ values and concentrations of NO_3^- in the precipitation of marine origin in this study indicate the influence of anthropogenic NO_x emissions (with relatively high $^{15}N/^{14}N$ ratio) locally and from neighboring large cities to the south of Guangzhou (e.g., Hong Kong, Shenzhen, Dongguan, and Zhongshan) on the temporal pattern of $\delta^{15}N$ of NO_3^-.

The $\delta^{15}N$ values of precipitation NO_3^- were obviously higher in the summer than in other seasons in 2009, and the pattern was different from that in 2008. Higher $\delta^{15}N$ values in atmospheric NO_3^- were often found in winter than in summer (e.g., Jülich, Germany, Freyer, 1978; 1991; Pretoria in South Africa, Heaton, 1987). These higher $\delta^{15}N$ values in winter have been attributed to N isotope exchange between NO and NO_2, which enriches ^{15}N in the more oxidized form. This N isotope exchange occurs more likely in the seasons when the NO_2/NO_x ratio and O_3 concentration is low, as demonstrated in the winter time at Jülich (Freyer et al., 1993). In the case of our study site in Guangzhou city, we found that in 2009 monthly mean NO_2/NO_x and O_3 concentration were lower in the summer than in the winter (Fig. 5). Thus low NO_2/NO_x and NO_x/O_3 ratios (favoring N isotopic exchange) in the summer of 2009 may partly explain relatively higher $\delta^{15}N$ in precipitation NO_3^- during the same time period (Fig. 2c). We don't have NO data for 2008. But we can infer that NO_2/NO_x ratio in 2008 will have a
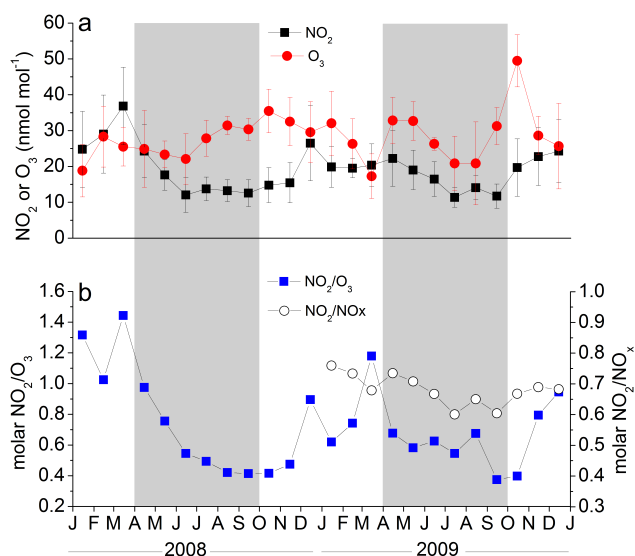
Fig. 5. Seasonal changes in NO_2 and O_3 concentrations **(a)**, monthly mean of three monitoring sites), molar ratios of NO_2/O_3 and NO_2/NO_x **(b)** during the study course in Guangzhou City. The shaded areas denote the warm seasons from April to September. Data is available at: http://www-app.gdepb.gov.cn/EQPublish/raqi.aspx).

Fig. 6. $\delta^{18}O$-NO_3^- **(a)** and $\delta^{15}N$-NO_3^- **(b)** vs. NO_3^- concentration in precipitation over the study period. For panel **(a)**, $R^2 = 0.21$, $P < 0.001$ in 2008; and $R^2 = 0.20$, $P = 0.001$ in 2009. For panel **(b)**, $R^2 = -0.03$, $P = 0.22$ in 2008; and $R^2 = 0.24$, $P < 0.001$ in 2009.

similar seasonal pattern as that in 2009, since NO_2 concentration was positively correlated to NO concentration in 2009 ($P < 0.001$, data not shown). However, in 2008, we found higher $\delta^{15}N$ values in precipitation NO_3^- in the winter, although the seasonal pattern was not as distinct as in 2009. So N isotopic exchange can not fully explain the observation in Guangzhou city.

We suggest that the difference in seasonal pattern of $\delta^{15}N$ of precipitation NO_3^- between 2008 and 2009 may have mainly resulted from two factors. One is the different precipitation regime. The study city Guangzhou, is located in the center of a large economic area (the Pearl River Delta), which consists of many big cities, like Guangzhou, Shenzhen, Zhuhai and Dongguan. The Pearl River Delta has an area of 4.2×10^4 km^2, where there are more than 0.4 billion habitants. During the strong precipitation events, especially typhoons, there is obvious air mass transportation from the east to the west in warm seasons (Fig. 3). There was a larger amount of precipitation in 2008 than in 2009, and precipitation was more concentrated in May and June (Fig. 2a), which thus might have blown N-bearing pollutants over the study city away and replaced the atmosphere with relatively clean air masses from the sea (Fig. 3). This is supported by the lower N input in precipitation in 2008 than in 2009 (Table 2) and the distinct seasonal fluctuation of precipitation NO_3^- in 2008 (Fig. 2b). The other is human activities. In 2008, many manufacturers in Guangzhou and the Pearl River Delta were severely affected by the global financial crisis starting from 2007. Nevertheless, the economy recovered and was stimu-
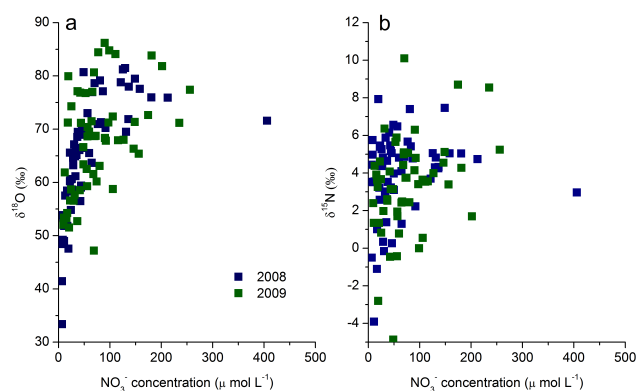
lated by the intensive preparations for the 16th Asian Games. The gross domestic product of Guangzhou City is 11.5% higher in 2009 than in 2008 (http://www.gemc.gov.cn/). In the present study, we observed significant correlations between $\delta^{15}N$ of NO_3^- and concentrations of NO_3^- (Fig. 6) and SO_4^{2-} (data not shown) in 2009, indicating the importance of air pollution in controlling $\delta^{15}N$ of precipitation NO_3^-. Such strong correlations have also been noted for precipitation across 33 sites in midwestern and northeastern US (Elliott et al., 2007).

4.3 Partitioning of NO_x sources using N isotopes of NO_3^-

The $\delta^{15}N$ values of fuel NO_x (e.g., from coal combustion) have been reported to be much more positive than those from natural sources, although a few studies showed negative values (Supplement). Furthermore, the fuel NO_x are generally more enriched in ^{15}N than the thermal NO_x (Supplement). Based on the positive $\delta^{15}N$ values in most of the samples in our study, we speculate that the source of NO_x is predominantly fossil fuel combustion in Guangzhou City, particularly coal combustion, because coal is commonly used to generate electricity in this economically developing zone. This view is further supported by a strong correlation of NO_3^- concentration with SO_4^{2-} concentration in precipitation (Fig. 7), which suggests that NO_x and SO_2 may be produced simultaneously through S-containing coal combustion as vehicles emit negligible SO_2 relative to coal combustion sources. A bottom-up inventory revealed that in China, more than 70% of the total NO_x emission was from coal combustion (Tian et al., 2001).

Assuming that the precipitation NO_3^- at our study site has only two sources, anthropogenic (assuming that NO_x emissions principally originate from fossil fuel combustion) and natural (e.g., lightning and biogenic emissions), and

that $\delta^{15}N_{anthropogenic}$ is +10.1‰ (the maximum value of the study period) and $\delta^{15}N_{natural}$ is −4.9‰ (the minimum value), we can attempt to separate the relative contribution of each source to the total NO_3^- deposition for each sampling event and each year using a simple two-end-member model. Calculations show that on average 59% and 55% of precipitation NO_3^- in 2008 and 2009, respectively, were from an anthropogenic source. This estimate is tentative because the variation of $\delta^{15}N$ of NO_3^- are also influenced by the ^{15}N partition within NO_x and/or the isotopic fractionation arising from the conversion of NO_2 to NO_3^- or the transport of atmospheric NO_3^- itself (Morin et al., 2009), which have not been considered in the above estimation. It is difficult to assess these uncertainties with the present data. However, such an estimate can provide an insight into the change in the contribution of anthropogenic emissions with time (Hastings et al., 2003, 2009).

The anthropogenic contribution to total NO_3^- deposition discussed above is likely underestimated because such a high NO_3^- deposition in the study city must directly result from increased anthropogenic emissions due to energy use from local cities in the Pearl River Delta where our study site is located and/or from inland cities in China. A bottom-up inventory conducted in the Pearl River Delta showed that 46% and 41% of the total NO_x emissions in 2006 were from power plant and mobile sources, respectively, and that the industry was responsible for an additional 12% (Zheng et al., 2009). In that inventory, however, the contributions of biogenic sources and lightning were not included (Zheng et al., 2009). A top-down inventory constructed using an inversion approach with a global 3-D chemical transport model (GEOS-Chem) showed that fossil fuel and biofuel combustion accounted for 77% and 12% of the total NO_x emissions over east China, respectively, and the rest (11%) was accounted for by biomass burning, microbial sources, and lightning (Wang et al., 2007). Several factors may lead to the underestimation on anthropogenic contribution to NO_x emission. First, the assumed $\delta^{15}N_{anthropogenic}$ value in this study may be higher than the actual one, as the thermal NO_x exhibits negative values in $\delta^{15}N$ and the $\delta^{15}N$ values of vehicular NO_x are reported around +5‰ (see the introduction or Supplement). Secondly, the $\delta^{15}N_{natural}$ value used in the estimation may be higher than the actual value, although it is very similar to the lowest record of −3.8‰ in rain NO_3^- in Hawaii (Carrillo et al., 2002). Thirdly, the ^{15}N signature of thermal NO_x (largely consisted of vehicle exhaust) might have failed to be recorded by our precipitation samples, for ground-level emissions of tailpipe NO_x relative to smokestack NO_x emissions higher in the troposphere may result in different reaction pathways and scavenging efficiencies for vehicle NO_x (Elliott et al., 2007).
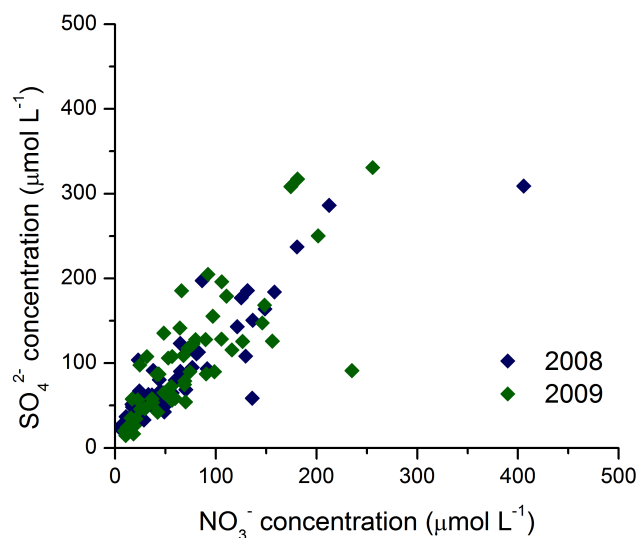

Fig. 7. NO_3^- concentration vs. SO_4^{2-} concentration in precipitation collected in 2008 to 2009 in Guangzhou City. $R^2 = 0.80$, $P < 0.001$ in 2008; $R^2 = 0.77$, $P < 0.001$ in 2009.

4.4 Oxygen isotopes of NO_3^-

In this study, $\delta^{18}O$ of precipitation NO_3^- ranged from +33.4 to +86.2‰, with an average of +66.3‰ (Table 1). These values lie within the broad range of previous reports (Hastings et al., 2003, 2007; Elliott et al., 2007, 2009; Kendall et al., 2007; Morin et al., 2008, 2009; Tsunogai et al., 2010). However, the annual mean values of $\delta^{18}O$ were lower than those of previous studies performed in high latitude and polar regions and our data fell in the low end of the reported range of the world.

The $\delta^{18}O$ values of atmospheric NO_3^- varied from +59.6 to +114.4‰ in coastal Antarctica (66°40′ S, 140°01′ E), with averages of +63.2‰ in January to March, +79.1‰ in March to mid-July, +103.9‰ in mid-July to September, and +77.2‰ in October to December (Savarino et al., 2007). In nonpolar regions, Morin et al. (2009) observed a large range of $\delta^{18}O$ values for atmospheric NO_3^- (+50 to +90‰) in their study for the Atlantic Ocean boundary layer from 65° S to 79° N. Similarly, a range of +67 to +100‰ for precipitation NO_3^- was observed in the island of Rishiri, northern Japan (45.2° N, Tsunogai et al., 2010). Our results are slightly lower than those reported for Bermuda, which has a low latitude (32.27° N, 64.87° W), where the $\delta^{18}O$ values of precipitation NO_3^- ranged from +60.3 to +86.5‰, averaging +68.6‰ in the warm season and +76.9‰ in the cool season (Hastings et al., 2003), across the region of Ohio, New York, and Pennsylvania in the US where the $\delta^{18}O$ values of NO_3^- ranged from +45.2 to +94.0‰ with mean values of +77.4‰ for HNO_3 vapor and +75.2‰ for particulate NO_3^- (Elliott et al., 2009), and the Gulf of Aqaba in Israel where aerosol NO_3^- ranged from +66.1 to +85.3‰, with +77.3‰

in the summer and +80.5‰ in the winter (Wankel et al., 2010). The relatively low $\delta^{18}O$ values in our study suggest the importance of the OH radical pathway in forming atmospheric NO_3^- (through which O_3 donates fewer O atoms to NO_3^- than that through the N_2O_5 pathway; see Introduction), due in part to the long summer time and maybe the strong solar radiation. This interpretation is consistent with the results obtained based on a global model of $\Delta^{17}O$ (the oxygen isotopic anomaly which is quantified as $\delta^{17}O–0.52 \times \delta^{18}O$) of atmospheric NO_3^-; NO_3^- production via the OH pathway predominates (up to 87%) in the tropics where OH concentration is the highest (Alexander et al., 2009).

The seasonality of these NO_3^- formation pathways is a function of both temperature (N_2O_5 is thermally decomposed) and solar radiation (OH is photolytically produced). This chemical fingerprint of $\delta^{18}O$ of NO_3^- by O_3 has been used to characterize the predominance of multiple chemical pathways (Savarino et al., 2007; Jarvis et al., 2008; Morin et al., 2008). In the present study, the warm season averages of +63.5‰ and +66.4‰ in 2008 and 2009, respectively, were significantly lower than the cool season averages of 73.2‰ and 73.0‰ (Table 2). As expected, temperature controls $\delta^{18}O$ of NO_3^- (Fig. 4a). When the air temperature was below 23 °C, $\delta^{18}O$ of NO_3^- was higher than 70‰. However, a large variation was noted when the temperature was above 23 °C. We found no relationship between $\delta^{18}O$ and solar radiation (data not shown). We initially expected that the seasonal fluctuation would be small due to the relatively equal distribution of daytime and nighttime within a day throughout the year as compared to high latitude and polar regions that have much longer nighttime in winter. However, we found that at our study site, the difference in seasonal maximum and minimum $\delta^{18}O$ is as much as 53‰, and this difference is even greater than the seasonal difference of about 30‰ in coastal Antarctica when the austral later winter and early spring was excluded because during that period NO_3^- sedimentation from polar stratospheric clouds results in particular high $\delta^{18}O$ values which is very different from the situation in other seasons (Savarino et al., 2007) and greater than those in middle and high latitude areas (Hastings et al., 2003; Elliott et al., 2009; Tsunogai et al., 2010). The reasons remain unclear and further research is required.

Using the minimum and maximum of $\delta^{18}O$ reported for O_3 (+90 to +122‰, Krankowsky et al., 1995; Johnston and Thiemens, 1997) and OH (typically between −15‰ to 0‰ over the Asian continent, see maps from the Global Network of Isotopes in Precipitation, International Atomic Energy Agency, available at: http://isohis.iaea.org), one can expect that the $\delta^{18}O$ value of atmospheric NO_3^- will fall between +55‰ (assuming 2/3 oxygen atoms from O_3 and 1/3 from OH) and +102‰ (assuming 5/6 oxygen atoms from O_3 and 1/6 from OH) (see Hastings et al., 2003).

In this study, we observed that 18 samples (16% of the total samples) had $\delta^{18}O$ values being lower than +55‰. The

lowest was +33‰ (Fig. 2d), which, so far, is among the lowest ever reported in the world. One may argue that the presence of NO_2^- interferes with the analyses of $\delta^{18}O$-NO_3^- and may result in some errors (Casciotti et al., 2002; Casciotti et al., 2007, also see the method section). After the correction of NO_2^- interference (+0‰ to +5.8‰), we still find that in this study there are 12 values being lower than the expected minimum.

As stated previously, the OH pathway and the N_2O_5 pathway are the main channels for atmospheric NO_3^- formation. Globally, 76% and 18% of annual inorganic NO_3^- are formed via the OH pathway and the N_2O_5 pathway, respectively, based on a global model of $\Delta^{17}O$ of atmospheric NO_3^- (Alexander et al., 2009). At night, NO_3 can also react with dimethylsulfide (DMS) or hydrocarbons (HC), termed the NO_3^- + DMS/HC pathway here; this pathway accounts for 4% of the annual inorganic NO_3^- on the global scale based on a global model of $\Delta^{17}O$ of atmospheric NO_3^- (Alexander et al., 2009). Atmospheric NO_3^- induced via the NO_3^- + DMS/HC pathway will probably have higher $\delta^{18}O$ values than those induced via the OH pathway and the N_2O_5 pathway due to its more involvement with O_3 during formation (Alexander et al., 2009). In addition, NO_x can interact with halogen oxides, such as bromine oxide (BrO), to form bromine nitrate ($BrONO_2$) and this in turn can be hydrolyzed to NO_3 (Morin et al., 2008; Alexander et al., 2009). The atmospheric NO_3^- induced by this pathway will have a $\delta^{18}O$ value similar to that of O_3, for BrO is expected to have a large $\delta^{18}O$ value due to the involvement of O_3 in BrO formation. Thus, the last two pathways cannot explain the $\delta^{18}O$ values of NO_3^- below +55‰ in our study either. One possibility for the lower than usual $\delta^{18}O$ values of NO_3^- is oxygen isotopic fractionation, which can induce large variations in $\delta^{18}O$ values between the reactants and the products (see e.g., Chakraborty and Chakraborty, 2003).

The other possible explanation is the reaction of NO with peroxy radicals (HO_2 and its organic homologues RO_2), which can compete with O_3 to convert NO into NO_2(Reactions R7 and R8).

$$OH + CO + O_2 \rightarrow CO_2 + HO_2 \quad \text{(R7)}$$

$$HO_2 + NO \rightarrow NO_2 + OH \quad \text{(R8)}$$
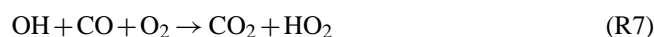
The $\delta^{18}O$ of peroxy radicals is expected to be much lower than that of O_3 as the O atoms should come from atmospheric O_2 ($\delta^{18}O$ = +23.9‰, see Barkan and Luz, 2003). If we assume that NO exchanges O atom to form NO_2 completely with peroxy radicals instead of O_3, then we can expect that the minimum $\delta^{18}O$ value of formed NO_3^- will be +11‰ followed by the reaction R3 (up to 2/3 of the O atoms from atmospheric O_2 and 1/3 from OH) and +28% followed by the reactions R4 to R6 (up to 4/6 of the O atom from atmospheric O_2, 1/6 from O_3 and 1/6 O from H_2O), respectively. We observed the lowest value of +33‰ in the study city, which is

just slightly higher than the calculated minimum of +28‰, suggesting that peroxy radicals may be an important oxidant in the conversion of NO to NO_2 and thereby NO_3^- formation in the atmosphere.

Peroxy radicals are important intermediates in atmospheric photo-oxidant formation. They arise from the oxidation of carbon monoxide (CO) and volatile organic compounds (VOC) by OH radicals, NO_3 radicals, halogen atoms, and O_3. This phenomenon very likely occurs in our study city that has complex air pollution, because CO is also a major air pollutant (Hua et al., 2008; Liu et al., 2008; Zhang et al., 2008a; Shao et al., 2009).

5 Conclusions

We demonstrated the seasonal variations of N and O isotopic composition of precipitation NO_3^- in Guangzhou, a severely N-polluted city in China, in an effort to better understand the spatial and seasonal variability of atmospheric NO_x sources and the formation pathways in this city. We can draw several conclusions from our observations. (1) Positive nitrate $\delta^{15}N$ values were observed throughout the year, indicating the importance of NO_x emissions from coal combustion. Different seasonal patterns of $\delta^{15}N$-NO_3^- were observed between 2008 and 2009, which might reflect different human activities associated with the global financial crisis and the intensive preparations for the 16th Asian Games. (2) The anthropogenic NO_x source accounted for 59% and 55% of the total precipitation NO_3^- input in 2008 and 2009, respectively, based on an isotope model. Nevertheless, this may be an underestimation. (3) The observed range of $\delta^{18}O$-NO_3^- values from +33.4‰ to +86.5‰ was lower than those reported for high altitude and polar areas, underscoring the importance of OH radicals in the formation of atmospheric NO_3^- due to the relative long summer. Sixteen percent of $\delta^{18}O$ values that were lower than the expected minimum of +55‰ at our study site likely resulted from the reaction of NO with peroxy radicals; peroxy radicals can compete with O_3 to convert NO to NO_2, thereby donate O atoms with much lower $\delta^{18}O$ values than that of O_3 to atmospheric NO_3^-.

Supplementary material related to this article is available online at:
http://www.atmos-chem-phys.net/11/1313/2011/
acp-11-1313-2011-supplement.pdf.

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