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

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Abstract. Nitric acid (HNO\textsubscript{3}) or nitrate (NO\textsubscript{3}\textsuperscript{−}) is the dominant sink for reactive nitrogen oxides (NO\textsubscript{x} = NO + NO\textsubscript{2}) in the atmosphere. In many Chinese cities, HNO\textsubscript{3} is becoming a significant contributor to acid deposition. In the present study, we measured nitrogen (N) and oxygen (O) isotopic composition of NO\textsubscript{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\textsubscript{x} sources and the NO\textsubscript{3} formation pathways in this N-polluted city in the Pearl River Delta region. The \(\delta^{15}\text{N}\) values of NO\textsubscript{3} (versus air N\textsubscript{2}) ranged from -4.9 to +10.1‰, and averaged +3.9‰ in 2008 and +3.3‰ in 2009. Positive \(\delta^{15}\text{N}\) values were observed throughout the year, indicating the anthropogenic contribution of NO\textsubscript{x} emissions, particularly from coal combustion. Different seasonal patterns of \(\delta^{15}\text{N}-\text{NO}_3\) 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 \(\delta^{18}\text{O}\) 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 \(\delta^{18}\text{O}\) 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\textsubscript{3} to convert NO to NO\textsubscript{2}, thereby donate O atoms with much lower \(\delta^{18}\text{O}\) value than that of O\textsubscript{3} to atmospheric NO\textsubscript{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\textsubscript{3} in a N-polluted city.

1 Introduction

Global atmospheric emissions of nitrogen oxides (NO\textsubscript{x}, the sum of NO and NO\textsubscript{2}) have increased dramatically during the past 150 years (Galloway et al., 2004, 2008). Current global NO\textsubscript{x} emissions are dominated by fossil fuel combustion (63%) and far exceed natural NO\textsubscript{x} sources, such as lightning, biogenic soil processes, and wildfires (Ehhalt et al., 2001). NO\textsubscript{x} contributes to the formation of ozone (O\textsubscript{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\textsubscript{x} is oxidized via several pathways to form highly soluble nitric acid (HNO\textsubscript{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\textsubscript{3} associated with increased NO\textsubscript{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\textsubscript{x} emissions is expected to have shifted from North America and Europe to Asia (Ehhalt et al., 2001). In China, HNO\textsubscript{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 (Ehnhall 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$_2$O$_5$) (Reaction R5). The hydrolysis of N$_2$O$_5$ yields HNO$_3$(g) (Reaction R6). This pathway is most prevalent during winter as N$_2$O$_5$ is thermally unstable (Calvert et al., 1985), and is termed the N$_2$O$_5$ pathway hereafter.

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad \text{(R1)} \]
\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \quad \text{(R2)} \]
\[ \text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3 \quad \text{(R3)} \]
\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad \text{(R4)} \]
\[ \text{NO}_3 + \text{NO}_2 \leftrightarrow \text{N}_2\text{O}_5 \quad \text{(R5)} \]
\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O}_{(\text{surface})} \rightarrow \text{HNO}_3 \quad \text{(R6)} \]

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 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$_3$) (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$_2$O$_5$ pathway reflects the contribution of up to 5/6 O$_3$ and 1/6 H$_2$O (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$_2$O$_5$ pathway. The N$_2$O$_5$ 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$_3$ 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$_3^-$, and NO$_2^-$, 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$_2$O 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 δ$^{13}$N of NO$_3^-$ and ±0.5‰ for δ$^{18}$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 δ$^{15}$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 anlyte NO$_2$O (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$_2$O generated from NO$_3^-$ deposition was reported to result in a mean lowering of the δ$^{15}$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$_2$O, the δ$^{15}$N values reported here represent the combined pools of NO$_3^-$ and NO$_2^-$.

The presence of NO$_3^-$ interferes with the analyses of δ$^{18}$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$_3^-$ concentrations were 3% of total NO$_3^-$ plus NO$_2^-$.

In our study, four rainwater samples contained more than 5 µmol L$^{-1}$ NO$_3^-$, 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 δ$^{18}$O of NO$_2^-$ is the same as δ$^{18}$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 δ$^{18}$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, δ$^{15}$N, and δ$^{18}$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 µmol L$^{-1}$, except for one rain event on 17 September 2008 that had an unusually high concentration (406 µmol 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, δ¹⁵N, and δ¹⁸O of NO₃⁻ in precipitation.

<table>
<thead>
<tr>
<th>Year</th>
<th>NO₃⁻ con. (µmol L⁻¹)</th>
<th>δ¹⁵N-NO₃⁻ (%)</th>
<th>δ¹⁸O-NO₃⁻ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range</td>
<td>Meanᵃ</td>
<td>Meanᵇ</td>
</tr>
<tr>
<td>2008</td>
<td>6 to 406</td>
<td>63</td>
<td>53</td>
</tr>
<tr>
<td>2009</td>
<td>9 to 256</td>
<td>77</td>
<td>68</td>
</tr>
</tbody>
</table>

ᵃ arithmetic mean.
ᵇ volume-weighted mean.
ᶜ NO₃⁻-flux-weighted mean.

Table 2. Seasonal comparison of concentration, δ¹⁵N, and δ¹⁸O of NO₃⁻ in precipitation.

<table>
<thead>
<tr>
<th>Year</th>
<th>Season</th>
<th>n</th>
<th>Precipitation input NO₃⁻ (kg N ha⁻¹ a⁻¹)</th>
<th>NO₃⁻ con. (µmol L⁻¹)</th>
<th>δ¹⁵N-NO₃⁻ (%)</th>
<th>δ¹⁸O-NO₃⁻ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(mm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2008</td>
<td>Cool</td>
<td>9</td>
<td>491</td>
<td>4.1</td>
<td>89.9 (9 to 181, 19.6)</td>
<td>+4.5 (+0.3 to +7.5, 0.7)</td>
</tr>
<tr>
<td></td>
<td>Warm</td>
<td>50</td>
<td>1670</td>
<td>11.9</td>
<td>57.7 (6 to 406, 9.4)</td>
<td>+3.8 (−3.9 to +7.9, 0.3)</td>
</tr>
<tr>
<td></td>
<td>P value</td>
<td></td>
<td></td>
<td>0.18</td>
<td>0.41</td>
<td>0.01</td>
</tr>
<tr>
<td>2009</td>
<td>Cool</td>
<td>11</td>
<td>411</td>
<td>3.7</td>
<td>67.6 (19 to 181, 14.5)</td>
<td>+0.7 (−4.9 to +4.3, 0.9)</td>
</tr>
<tr>
<td></td>
<td>Warm</td>
<td>43</td>
<td>1520</td>
<td>14.8</td>
<td>78.8 (10 to 256, 9.1)</td>
<td>+4.1 (+0.5 to +10.1, 0.3)</td>
</tr>
<tr>
<td></td>
<td>P value</td>
<td></td>
<td></td>
<td>&lt;0.001</td>
<td>0.05</td>
<td></td>
</tr>
</tbody>
</table>

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.

3.2 N isotopes of NO₃⁻

Our measurements of δ¹⁵N of precipitation NO₃⁻ 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 δ¹⁵N values were observed throughout the year, 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 δ¹⁵N values between continental and marine sources (Table 3). In 2009, δ¹⁵N of NO₃⁻ in the warm season was significantly higher than that in the cool season (Table 2).

3.3 O isotopes of NO₃⁻

The δ¹⁸O values of NO₃⁻ ranged from +33.4 to +86.2‰ (Fig. 2d), with annual mean values of +65.0‰ and +76.7‰ in 2008 and 2009, respectively (Table 1). The NO₃⁻-flux-weighted δ¹⁵N values were +71.8‰ in 2008 and +70.6‰ in 2009 (Table 1). The seasonal pattern of δ¹⁸O of NO₃⁻ was clear, with values reaching a maximum in July or August. As a result, the δ¹⁸O values of NO₃⁻ were significantly higher in the cool season than in the warm season for both study years.
Table 3. Sources comparison of concentration, $\delta^{15}$N, and $\delta^{18}$O of NO$_3^-$ in precipitation.

<table>
<thead>
<tr>
<th>Year</th>
<th>Season</th>
<th>$n$</th>
<th>Precipitation (mm)</th>
<th>NO$_3^-$ input (kg N ha$^{-1}$ a$^{-1}$)</th>
<th>NO$_3^-$ con. (µmol L$^{-1}$)</th>
<th>$\delta^{15}$N-NO$_3^-$ (%)</th>
<th>$\delta^{18}$O-NO$_3^-$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2008</td>
<td>Continental</td>
<td>21</td>
<td>824</td>
<td>8.4</td>
<td>95.2 (9 to 406, 19.0)</td>
<td>+3.4 (--3.9 to +7.4, 0.6)</td>
<td>+71.6 (+51.8 to +81.5, 1.9)</td>
</tr>
<tr>
<td></td>
<td>Marine</td>
<td>38</td>
<td>1337</td>
<td>7.6</td>
<td>44.5 (6 to 212, 6.9)</td>
<td>+4.2 (--1.1 to +7.9, 0.3)</td>
<td>+61.3 (+33.4 to +79.5, 1.6)</td>
</tr>
<tr>
<td>P value</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.004</td>
<td>0.22</td>
</tr>
<tr>
<td>2009</td>
<td>Continental</td>
<td>19</td>
<td>589</td>
<td>8.3</td>
<td>83.1 (12 to 202, 13.0)</td>
<td>+1.9 (--4.9 to +8.7, 0.7)</td>
<td>+71.6 (+58.8 to +84.8, 1.9)</td>
</tr>
<tr>
<td></td>
<td>Marine</td>
<td>35</td>
<td>1342</td>
<td>12.1</td>
<td>73.0 (10 to 256, 9.8)</td>
<td>+4.1 (+1.1 to +10.1, 0.3)</td>
<td>+65.5 (+47.2 to +86.2, 1.7)</td>
</tr>
<tr>
<td>P value</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.53</td>
<td>0.002</td>
<td>0.06</td>
</tr>
</tbody>
</table>

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.

The continental source precipitation had higher $\delta^{18}$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 $\delta^{15}$N of precipitation NO$_3^-$ over the study period varied between $-4.9\%e$ and $+10.1\%e$, with a total arithmetic mean of $+3.6\%e$ (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 $\delta^{15}$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, δ15N 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 δ15N 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 δ15N data from different atmospheric matrices, because the δ15N of aerosol NO−3 is very different from that of rainwater NO−3 in some studies (e.g., aerosol nitrate δ15N was 9‰ higher than rainwater nitrate δ15N in Jülich, a moderately polluted city of Germany; 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 δ15N seems to vary from site to site. In a study performed in the Arctic, temperature was found to be a major determinant of δ15N-NO−3 values in all seasons except spring when snowpack emissions are maximal (Morin et al., 2008). Temperature was also found to significantly influence δ15N-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), δ15N 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 NOx sources for those studies. In the present study, δ15N-NO−3 was correlated with temperature only in 2009 (Fig. 4b). The high δ15N-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 δ15N values of NO−3 to those reported for the atmospheric matrices collected above oceans. The δ15N 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 δ15N 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 δ15N of rain NO−3 in Bermuda in the North Atlantic Ocean (Hastings et al., 2003). The δ15N 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 most values were positive during the study period (Fig. 2c). Furthermore, we found that the averaged δ15N values were lower for precipitation from the continent than for that from the sea, particularly in 2009 (Table 3). Over the two study years, δ15N 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 μmol L−1 in 2008 and 2009, respectively, Table 3) was far higher than the annual means (0.5 to 2 μmol L−1) in Hawaii (Carrillo et al., 2002). The high δ15N values and concentrations of NO−3 in the precipitation of marine origin in this study indicate the influence of anthropogenic NOx emissions (with relatively high 15N/14N 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 δ15N of NO−3.

The δ15N 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 δ15N 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 δ15N values in winter have been attributed to N isotope exchange between NO and NO2, which enriches 15N in the more oxidized form. This N isotope exchange occurs more likely in the seasons when the NO3/NOx ratio and O3 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 NO2/NOx and O3 concentration were lower in the summer than in the winter (Fig. 5). Thus low NO2/NOx and NOx/O3 ratios (favoring N isotopic exchange) in the summer of 2009 may partly explain relatively higher δ15N in precipitation NO−3 during the same time period (Fig. 2c). We don’t have NO data for 2008. But we can infer that NO2/NOx ratio in 2008 will have a
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, Zuhai and Dongguan. The Pearl River Delta has an area of $4.2 \times 10^4$ km$^2$, where there are more than 0.4 billion inhabitants. 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 stimulated 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

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*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 (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.*
that $\delta^{15}N_{\text{anthropogenic}}$ is $+10.1\%e$ (the maximum value of the study period) and $\delta^{15}N_{\text{natural}}$ is $-4.9\%e$ (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 $\delta^{15}N_{\text{anthropogenic}}$ 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 $+5\%e$ (see the introduction or Supplement). Secondly, the $\delta^{15}N_{\text{natural}}$ value used in the estimation may be higher than the actual value, although it is very similar to the lowest record of $-3.8\%e$ 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.](image-url)

### 4.4 Oxygen isotopes of NO$_3^-$

In this study, $\delta^{18}O$ of precipitation NO$_3^-$ ranged from $+33.4$ to $+86.2\%e$, with an average of $+66.3\%e$ (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 $+114.4\%e$ in coastal Antarctica ($66^\circ 40'\ S$, $140^\circ 01'\ E$), with averages of $+63.2\%e$ in January to March, $+79.1\%e$ in March to mid-July, $+103.9\%e$ in mid-July to September, and $+77.2\%e$ in October to December (Savarin 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 $+90\%e$) in their study for the Atlantic Ocean boundary layer from $65^\circ S$ to $79^\circ N$. Similarly, a range of $+67$ to $+100\%e$ for precipitation NO$_3^-$ was observed in the island of Rishiri, northern Japan ($45.2^\circ N$, Tsunogai et al., 2010). Our results are slightly lower than those reported for Bermuda, which has a low latitude ($32.27^\circ N$, $64.87^\circ W$), where the $\delta^{18}O$ values of precipitation NO$_3^-$ ranged from $+60.3$ to $+86.5\%e$, averaging $+68.6\%e$ in the warm season and $+76.9\%e$ 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 $+94.0\%e$ with mean values of $+77.4\%e$ for HNO$_3$ vapor and $+75.2\%e$ for particulate NO$_3^-$ (Elliott et al., 2009), and the Gulf of Aqaba in Israel where aerosol NO$_3^-$ ranged from $+66.1$ to $+85.3\%e$, with $+77.3\%e$...
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$_2$O$_5$ 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$_2$O$_3$ 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‰, Kranckowski 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$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$ pathway due to its more involvement with O$_3$ during formation (Alexander et al., 2009). In addition, NO$_3$ 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).

$$\text{OH} + \text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{HO}_2 \quad (\text{R7})$$

$$\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH} \quad (\text{R8})$$

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$_2^-$ 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$_2$O), 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 NO₃ and thereby NO₃⁻ 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, NO₃ radicals, halogen atoms, and O₃. 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 NO₃⁻ in Guangzhou, a severely N-polluted city in China, in an effort to better understand the spatial and seasonal variability of atmospheric NOₓ sources and the formation pathways in this city. We can draw several conclusions from our observations. (1) Positive nitrate δ¹⁵N values were observed throughout the year, indicating the importance of NOₓ emissions from coal combustion. Different seasonal patterns of δ¹⁵N-NO₃⁻ 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 NOₓ source accounted for 59% and 55% of the total precipitation NO₃⁻ input in 2008 and 2009, respectively, based on an isotope model. Nevertheless, this may be an underestimation. (3) The observed range of δ¹⁸O-NO₃⁻ 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 NO₃⁻ due to the relative long summer. Sixteen percent of δ¹⁸O 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 O₃ to convert NO to NO₂, thereby donate O atoms with much lower δ¹⁸O values than that of O₃ to atmospheric NO₃⁻.

Supplementary material related to this article is available online at:

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