Atmos. Chem. Phys. Discuss., 10, 21439–21474, 2010
www.atmos-chem-phys-discuss.net/10/21439/2010/
doi:10.5194/acpd-10-21439-2010

Atmospheric Chemistry and Physics Discussions

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

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Received: 4 September 2010 – Accepted: 6 September 2010 – Published: 8 September 2010

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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 used the denitrifier method to measure 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 altitude and polar areas. Several $\delta^{18}O$ values were observed lower than the expected minimum of 50‰ 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 contribute to the formation of ozone (O_3) and particulate matter (Ehhalt et al., 2001) and are thus an important factor affecting regional air quality and radiative balance (Morin et al., 2008). Once emitted to the atmosphere, NO_x are 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 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 population and power plants (Zhang 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 control 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 (Morin et al., 2008). The identification of NO_x sources to any given location is also vital to developing sound regulatory management and mitigation strategies for air and water quality (Elliott et al., 2007, 2009).

Once released to the atmosphere, NO_x are converted to atmospheric NO_3^- through a number of chemical pathways (Calvert et al., 1985; Heaton et al., 2004; also see Hastings et al., 2003, 2004; Elliott et al., 2007, 2009; Kendall et al., 2007; Morin et al., 2008, 2009). Most tropospheric NO_x are emitted as NO, which photochemically equilibrates 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.

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{R1}$$

$$NO_2 + h\nu \rightarrow NO + O \tag{R2}$$

$$NO_2 + OH \rightarrow HNO_3 \tag{R3}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{R4}$$

$$NO_3 + NO_2 \rightarrow N_2O_5 \tag{R5}$$

$$N_2O_5 + H_2O_{(surface)} \rightarrow 2HNO_3 \tag{R6}$$

Nitrogen stable isotopic composition has 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). The $\delta^{15}N$

values of anthropogenic and natural NO_x sources vary over a large range. The $\delta^{15}N$ values of NO_x from coal-fired power plants range from +5 to +13‰ (Heaton, 1990; Kiga et al., 2000), whereas vehicular NO_x emissions from tailpipe exhaust, roadside denuders, and roadside vegetation have relatively low $\delta^{15}N$ values (+3.7, +5.7, and +3.8‰, respectively) (Moore, 1977; Ammann et al., 1999; Pearson et al., 2000). One study also reported negative $\delta^{15}N$ values of NO_x for vehicle exhaust (e.g., −13 to −2‰, Heaton, 1990). 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).

On the other hand, $\delta^{18}O$ 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 O_3 (+90 to +120%) 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 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 5/6 O_3 and 1/6 H_2O. 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 can well explain the higher $\delta^{18}O$ of atmospheric

NO_3^- in winter than in summer in the 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; Morin et al., 2008, 2009). For instance, Elliott et al. (2007) demonstrated a strong correlation between wet deposition δ^{15}N-NO_3^- and stationary source (e.g., power plant facilities) NO_x emissions in the northeastern US, with higher δ^{15}N values (up to +3.2‰) found in areas affected by higher NO_x emissions, suggesting that the dual 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 δ^{15}N-NO_3^- in precipitation with lower values in the warm season due to the more proportional contribution of biogenic sources (e.g., lightning and 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, δ^{15}N-NO_3^- values would be higher than those of other remote areas; 3) δ^{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., 2007, 2009), but the seasonal variation would be small compared to those of high latitude and polar areas; and 4) δ^{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 Southern 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 nmoles 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 $\delta^{18}O$.

Because atmospheric NO_3^- likely contains a large mass-independent ^{17}O anomaly (Michalski et al., 2003, 2004), use of the denitrifier method for $\delta^{15}N$ measurements 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 lowing 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

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which NO_2^- concentrations were 3% of total NO_3^- plus NO_2^-. In our study, four rainwater samples contained more than 5 µmol 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. Thus, we expect 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-h 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 above ground level. This 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 (1.2 days) than in the summer (0.27 days), 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 h 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 for they passed through the South China Sea.

2.4 Calculations and statistical analysis

Annual precipitation N is the sum of the product of concentration and water amount for each sampling period. 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 (404 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% fallen during the warm season (Figs. 2a, 3; 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% fallen in the warm season (Table 2). Continental precipitation accounted for 38% and 31% of the annual precipitation amount in 2008 and 2009, 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. 2, 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 (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} yr^{-1} in 2008 and 21.8 kg N ha^{-1} yr^{-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} yr^{-1} in 2008 and 2009, respectively. Compared with the small measured N deposition of 1.8-3.2 kg N ha^{-1} yr^{-1} in some remote areas in China (Liu et al., 1993) and of 0.9 kg N ha^{-1} yr^{-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 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 (Table 4). 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 polar regions (Table 4), 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, δ^{15}N of wet NO_3^- deposition ranged from −8.1 to +3.2‰, with a mean of −1.5‰ (Elliott et al., 2007, Table 4). A wider range of δ^{15}N of atmospheric NO_3^- was observed in Europe (Freyer, 1978, 1991; Yeatman et al., 2001; Widory, 2007).

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 δ^{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 δ^{15}N-NO_3^- values in all seasons except spring when snowpack emissions are maximal (Morin et al., 2008). Temperature was also found to influence significantly δ^{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), δ^{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, δ^{15}N-NO_3^- was correlated with temperature only in 2009 (Fig. 5b). The high δ^{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).

The δ^{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 δ^{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 δ^{15}N of rain NO_3^- in Bermuda in the North Atlantic Ocean (Hastings et al., 2003). The δ^{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). In the present study, we initially expected that the precipitation samples collected from the sea would have similar δ^{15}N values of NO_3^- to those reported above.

We did observe a few negative values during storms in the summer of 2008, but most values were positive during the study period (Fig. 2). Furthermore, we found that the averaged δ^{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, δ^{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 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 δ^{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 $^{15}N/^{14}N$ 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. This difference in seasonal pattern between 2008 and 2009 may have resulted from two factors. One is the different precipitation regime; there was a larger amount of precipitation in 2008 than in 2009, and precipitation was concentrated in May and June, which might have blown N-bearing pollutants over the study city away and replaced the atmosphere with relatively clean air masses. This is supported by the lower N input in precipitation in 2008 than in 2009 (Table 2) and the clear seasonal fluctuation of precipitation NO_3^- in 2008. The other is human activity. 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 strong 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 Partition of NO_x sources using N isotopes of NO_3^-

The $\delta^{15}N$ values of NO_x from anthropogenic sources (e.g., fossil fuel combustion) have been reported to be much more positive than those from natural sources, although a few studies showed negative values (Table 4). Furthermore, NO_x from coal power plants are generally more enriched in ^{15}N than those from vehicle exhausts (Table 4). 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 speculation is further supported by a strong correlation of NO_3^- concentration with SO_4^{2-} concentration in precipitation (Fig. 4), 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).

If we assume that the precipitation NO_3^- at our study site has only two sources, anthropogenic (NO_x emissions principally from fossil fuel combustion) and natural (e.g., lightning and biogenic emissions), and that $\delta^{15}N_{\text{anthropogenic}}$ is +10.1‰ (the maximum value of the study period) and $\delta^{15}N_{\text{natural}}$ 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 the simple two-end-member model. Calculations show that 59% and 55% of precipitation NO_3^- in 2008 and 2009, respectively, were from an anthropogenic source. However, this estimate is tentative; atmospheric NO_3^- originates from the oxidation of NO and variations in the $\delta^{15}N$ values of NO_3^- may reflect the variation of $\delta^{15}N$ of source NO_x, but 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). 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).

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. The assumed $\delta^{15}N_{\text{anthropogenic}}$ value may be higher than the actual one, as NO_x emitted from fuel combustion (both coal combustion and vehicle exhaust) also have negative values (Table 4). Meanwhile, 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‰ in rain NO_3^- in Hawaii (Carrillo et al., 2002). 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).

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). Relatively low values were reported for $\delta^{18}O$ of atmospheric NO_3^- using the $AgNO_3^-$ method (non-denitrifier) compared to those using the denitrifier method (for more details, see Kendall et al., 2007). The values obtained in the present study lie within the broad range of previously reported values obtained with the same method as what we used (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). A range of +67 to +100‰ 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 δ^{18}O values of 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), and across the region of Ohio, New York, and Pennsylvania in the U.S. where the δ^{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). The relatively low δ^{18}O values in our study suggest the importance of the OH radical pathway in forming atmospheric NO_3^- (through which O_3 donates less 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 speculation is consistent with the results obtained based on a global model of Δ^{17}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 δ^{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 higher than the cool season averages of 73.2‰ and 73.0‰ (Table 2). As expected, temperature well controls δ^{18}O of NO_3^- (Fig. 5a). When air temperature was below 23°C, δ^{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 δ^{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 δ^{18}O is as much as 53‰, and this difference is very similar to the seasonal difference of 54‰

in coastal Antarctica (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‰) and OH (−30 to +2‰), one can expect that the $\delta^{18}O$ value of atmospheric NO_3^- will fall between +50‰ (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 a few $\delta^{18}O$ values that were lower than +50‰, with the lowest being +33‰ (Fig. 1d). This, so far, is among the lowest ever reported in the world.

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^-. At night, NO_3 can also react with dimethylsulfide (DMS) or hydrocarbons (HC), termed the DMS/HC pathway here. This pathway accounts for 4% of the annual inorganic NO_3^- on the global scale. Atmospheric NO_3^- induced via the DMS/HC pathway will probably have higher $\delta^{18}O$ values than those induced via the OH pathway and the N_2O_5 pathway. 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). This pathway is particularly important in polar areas in spring when photochemically driven emissions of reactive N from the snowpack into the atmosphere make the local oxidation of NO_x by bromine oxide the major contributor to the NO_3^- budget (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 +50‰ in our study.

One possible explanation for the low $\delta^{18}O$ values of NO_3^- 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).

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

$$HO_2 + NO \rightarrow NO_2 + OH \quad (R8)$$

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. 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 ($\delta^{18}O = +23.5‰$, see Hastings et al., 2003). 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 $\delta^{15}N\text{-}NO_3^-$ were observed between 2008 and 2009, which reflected 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 $\delta^{18}O\text{-}NO_3^-$ 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. Several $\delta^{18}O$ values that were lower than the expected minimum of +50‰ 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^-.

Acknowledgements. This work was supported by the National Natural Science Foundation of China (Nos. 30725006, 40703030, 30972365, U0833001, and 40875076), Guangdong Natural Science Foundation of China (No. 8151065005000016), a grant-in-aid for scientific research from Japan Society for Promotion of Science (JSPS) (No. 21310008), Grant for Projects for the Protection, Preservation & Restoration of Cultural Properties in Japan by The Sumitomo Foundation, Grants-in-Aid for Creative Scientific Research (Nos. 18380093 and 20780113), the Program to Create an Independent Research Environment for Young Researchers from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and the National Program on Key Basic Research Project of China (No. 2010CB428504). Y. T. Fang was supported by the JSPS with a Postdoctoral Fellowship for Foreign Researchers and a grant-in-aid for JSPS Fellows (No. 20-08421). We acknowledge Qiaojun Chen for drawing the backward air mass trajectories.

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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[c]	Range	Mean[a]	Mean[c]
2008	6~406	63	53	−3.9~+7.9	+3.9	+4.2	+33.4~+81.5	+65.0	+71.8
2009	9~256	77	68	−4.9~+10.1	+3.3	+3.5	+48.2~+86.2	+67.7	+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} yr^{-1})	Mean NO_3^- con. (µmol L^{-1})	Mean δ^{15}N-NO_3^- (‰)	Mean δ^{18}O-NO_3^- (‰)
2008	Cool	9	491	4.1	89.9 (19.6)	+4.5 (0.7)	+73.2 (3.2)
	Warm	50	1670	11.9	57.7 (9.4)	+3.8 (0.3)	+63.5 (1.4)
	P value				0.18	0.41	0.01
2009	Cool	11	411	3.7	67.6 (14.5)	+0.7 (0.9)	+73.0 (2.7)
	Warm	43	1520	14.8	78.8 (9.1)	+4.1 (0.3)	+66.4 (1.5)
	P value				0.57	< 0.001	0.05

The *P* values were obtained by one-way ANOVA performed for each study year. Standard errors of means in parentheses. Arithmetic means were used.

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

Year	Source	*n*	Precipitation (mm)	NO_3^- input (kg N ha^{-1} yr^{-1})	Mean NO_3^- con. (µmol L^{-1})	Mean δ^{15}N-NO_3^- (‰)	Mean δ^{18}O-NO_3^- (‰)
2008	Continental	21	824	8.4	95.2 (19.0)	+3.4 (0.6)	+71.6 (1.9)
	Marine	38	1337	7.6	44.5 (6.9)	+4.2 (0.3)	+61.3 (1.6)
	P value				0.004	0.22	<0.001
2009	Continental	19	589	8.3	83.1 (13.0)	+1.9 (0.7)	+71.6 (1.9)
	Marine	35	1342	12.1	73.0 (9.8)	+4.1 (0.3)	+65.5 (1.7)
	P value				0.53	0.002	0.06

The *P* values were obtained by one-way ANOVA. Standard errors of means in parentheses. Arithmetic means were used.

Table 4. $\delta^{15}N$ in NO_x sources and atmospheric NO_3^-.

	NO_x	NO_3^-	Ref.
Precipitation in Guangzhou, Guangdong, China		−4.9 to +10.1 (+3.6)	This study
Precipitation in Dinghushan, Guangdong, China		+0.7 to +11.1 (+5.0)	Koba et al., 2010
Precipitation in Guiyang, China		−3.8 to +8.4	Xiao and Liu, 2002
Precipitation in two suburban sites in Beijing, China		−4.6 to +20.7 (+1.7 and +6.8,)	Zhang et al., 2008b
Precipitation in two rural sites in Hebei, China		−10.0 to +6.9 (−1.4 and −1.0)	Zhang et al., 2008b
Precipitation in one rural site in Beijing, China		−4.5 to +22.0 (+1.4)	Zhang et al., 2008b
Precipitation in Wakayama, Japan		−7 to +14.5 (+3.2)	Tobari et al., 2010
Precipitation in Niigata, Japan		−8 to +2	Fukuzaki and Hayasaka, 2009
Precipitation in Toyama, Japan		−7.8 to +1.6	Wu et al., 2008
Precipitation in Tokyo, Japan		−5.8 to +3.9 (−1.2)	Kurata, 2002
Precipitation in Rishiri Island, Japan		−10 to +11	Tsunogai et al., 2010
Precipitation across the MW and NE US		−8.1 to +3.2 (−1.5)	Elliott et al., 2007
Precipitation in Hawaii (Pacific Ocean)		−3.8 to +2.4	Carrillo et al., 2002
Precipitation in Bermuda (Atlantic)		−13.9 to +1.8	Hastings et al., 2003
Aerosol over Atlantic Ocean (non-polar areas)		−7.1 to −1.6 (−4)	Morin et al., 2009
Aersol in Ny-Ålesund (Arctic)		−22.8 to −6.0 (−15)	Morin et al., 2009
Aerosol over Weddell sea (Antarctic)		−42.8 to 1.8 (−17)	Morin et al., 2009
Aerosol at Alert, Canada (Arctic)		−42 to +3	Morin et al., 2008
Aerosol at French Antarctic Station Dumont d'Urville (Antarctic)		−46.9 to +10.8	Savario et al., 2007
Natural gas combustion	+2.9 to +15.4		Widory, 2007
Diesel combustion	+3.9 to +5.4		Widory, 2007
Coal combustion	+4.8 to +9.6		Kiga et al., 2000
Coal-fired boiler	+6 to +13		Heaton, 1990
Vehicle exhaust	+3.9 to +5.4		Widory, 2007
Vehicle exhaust	+5.7		Ammann et al., 1999
Vehicle exhaust	+3.7		Moore, 1997
Vehicle exhaust	+3.8		Pearson et al., 2000
Fuel oil combustion	−19.4 to +2.9		Widory, 2007
Coal combustion	−5.3		Widory, 2007
Vehicle exhaust	−13 to −2		Heaton, 1990
Lightning (Lab. simulation)	−0.5 to +1.4		Hoering, 1957
NO from agriculture soils in Guangzhou	−48 to −20		Li and Wang 2008

Mean values appear in parentheses.

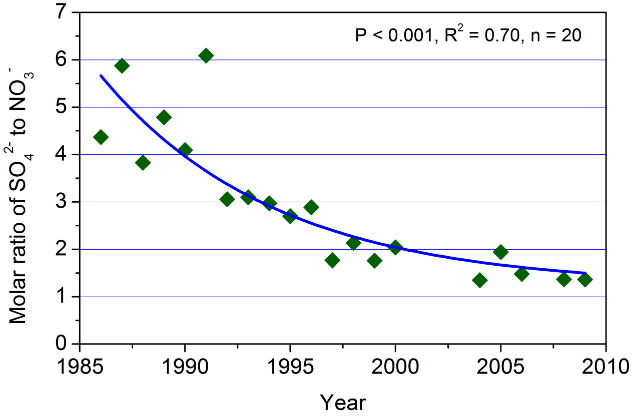

Fig. 1. Molar ratios of SO_4^{2-} to NO_3^- in precipitation in Guangzhou City during the period from 1986 to 2009. Data are from Quan et al. (1992) for 1986 to 1990, Ye et al. (2008) for 1991 to 2000, Liu et al. (2006) for 2004, Huang et al. (2009) for 2005, Cao et al. (2009) for 2006, and this study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

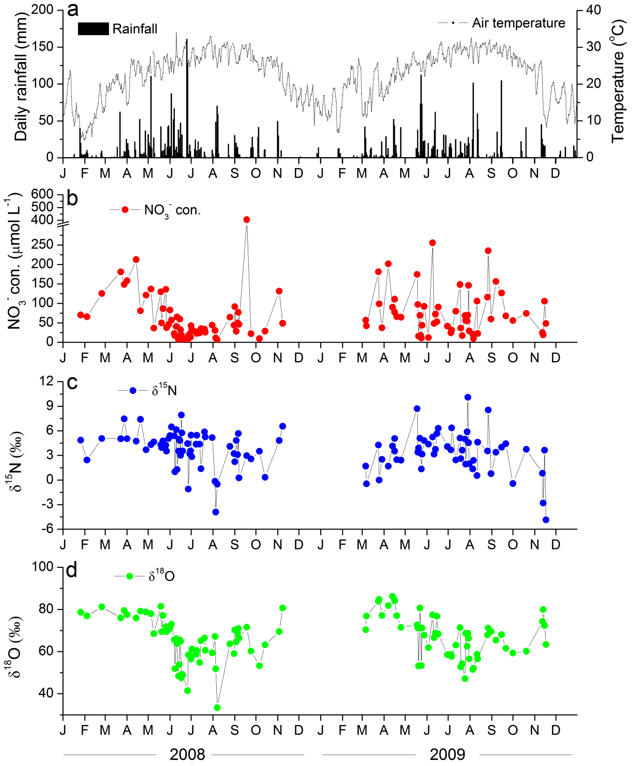

Fig. 2. Daily precipitation and mean air temperature **(a)**, NO_3^- concentration **(b)**, δ^{15}N-NO_3^- **(c)**, and δ^{18}O-NO_3^- **(d)** in precipitation from 2008 through 2009 in Guangzhou City.

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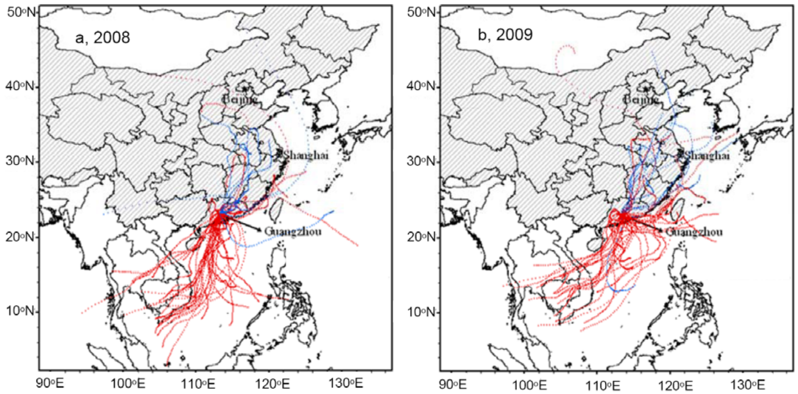

Fig. 3. 72-h air mass backward trajectories for all sampling days in Guangzhou City, based on NOAA HYSPLIT model back trajectories. Lines in blue denote air mass trajectories occurring in the cool season and those in red denote trajectories in the warm season.

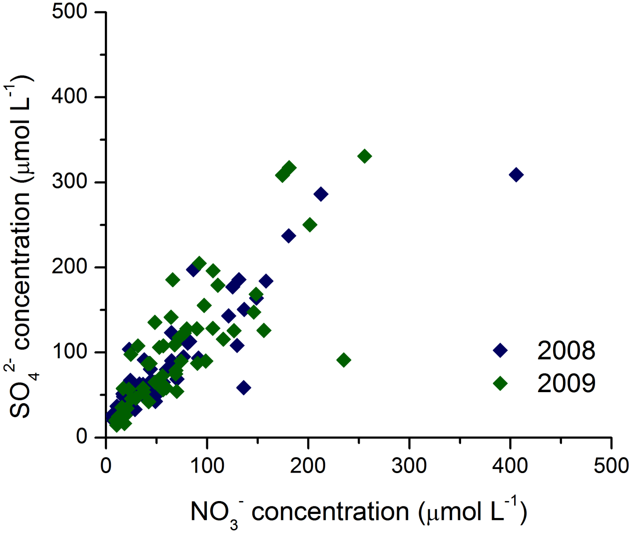

Fig. 4. NO_3^- concentration vs. SO_4^{2-} concentration in precipitation collected in 2008 to 2009 in Guangzhou City. $R^2 = 0.80$, $P<0.001$ in 2008; $R^2 = 0.77$, $P<0.001$ in 2009.

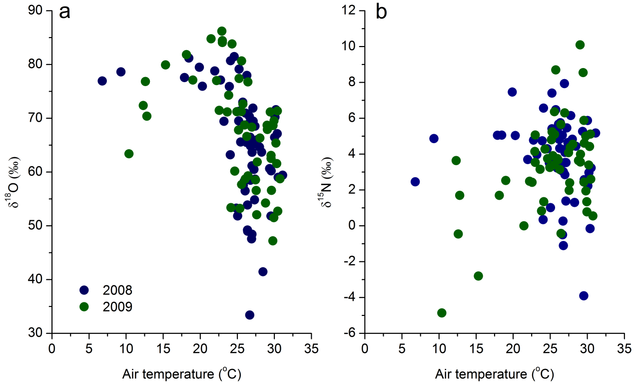

Fig. 5. δ^{18}O-NO_3^- **(a)** and δ^{15}N-NO_3^- **(b)** vs. mean air temperature three days prior to sampling over the 2008-2009 study period. For panel a, $R^2 = -0.21$, $P<0.001$ in 2008; and $R^2 = -0.20$, $P = 0.001$ in 2009. For panel b, $R^2 = -0.03$, $P = 0.222$ in 2008; and $R^2 = 0.24$, $P<0.001$ in 2009.

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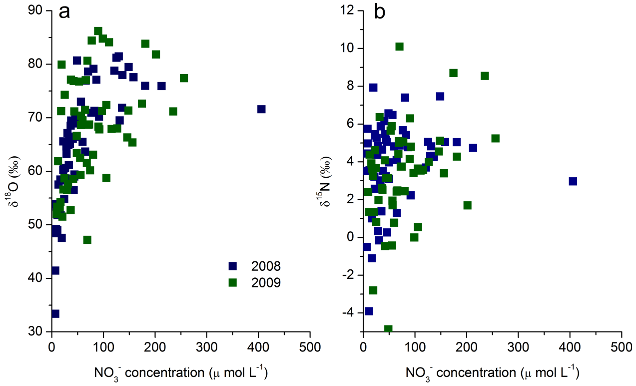

Fig. 6. δ^{18}O-NO_3^- **(a)** and δ^{15}N-NO_3^- **(b)** vs. NO_3^- concentration in precipitation over the 2008–2009 study period. For panel a, $R^2 = 0.21$, $P<0.001$ in 2008; and $R^2 = 0.20$, $P = 0.001$ in 2009. For panel b, $R^2 = -0.03$, $P = 0.22$ in 2008; and $R^2 = 0.24$, $P< 0.001$ in 2009.