Atmospheric $\Delta^{17}O(NO_3^-)$ reveals nocturnal chemistry dominates nitrate production in Beijing haze

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Abstract. The rapid mass increase of atmospheric nitrate is a critical driving force for the occurrence of fine-particle pollution (referred to as haze hereafter) in Beijing. However, the exact mechanisms for this rapid increase of nitrate mass has been not well constrained from field observations. Here we present the first observations of the oxygen-17 excess of atmospheric nitrate ($\Delta^{17}O(NO_3^-)$) collected in Beijing haze to reveal the relative importance of different nitrate formation pathways, and we also present the simultaneously observed $\delta^{15}N(NO_3^-)$. During our sampling period, 12h-averaged mass concentrations of $PM_{2.5}$ varied from 16 to 323 μg m^{-3} with a mean of (141±88 (1SD)) μg m^{-3}, with nitrate ranging from 0.3 to 106.7 μg m^{-3}. The observed $\Delta^{17}O(NO_3^-)$ ranged from 27.5 ‰ to 33.9 ‰ with a mean of (30.6±1.8) ‰ while $\delta^{15}N(NO_3^-)$ ranged from –2.5 ‰ to 19.2 ‰ with a mean of (7.4±6.8) ‰. $\Delta^{17}O(NO_3^-)$-constrained calculations suggest nocturnal pathways ($N_2O_5 + H_2O/Cl^-$ and NO_3 + HC) dominated nitrate production during polluted days ($PM_{2.5} \geq 75$ μg m^{-3}) with the mean possible fraction of 56 – 97 %. Our results illustrate the potentiality of $\Delta^{17}O$ in tracing nitrate formation pathways, future modelling work with the constraint of isotope data reported here may further improve our understanding of nitrogen cycle during haze.

1 Introduction

Severe and frequent haze pollution has become a crucial threat for the air quality in megacity Beijing and the North China Plain in recent years. The high concentrations of $PM_{2.5}$ (particulate matter with an aerodynamic diameter equal or less than 2.5 μm) during severe haze, of which the hourly average can reach 1000 μg m^{-3} (Zheng et al., 2015a), is harmful to the public health by contributing to cardiovascular morbidity and mortality (Cheng et al., 2013; Brook et al., 2010). Nitrate is an important component of $PM_{2.5}$, accounting for 1–45 % of $PM_{2.5}$ mass in Beijing and North China Plain (Wen et al., 2015; Zheng et al., 2015a; Zheng et al., 2015b). The main formation pathways of atmospheric nitrate, defined herein as gas-phase HNO_3 plus particulate NO_3^-, in urban area are summarized in Fig. 1, which includes: (i) NO_2 oxidation by OH radical in the gas-phase, (ii) heterogeneous uptake of NO_2 on wet aerosols, (iii) NO_3 radical reacting with hydrocarbon (HC), and (iv) heterogeneous uptake of N_2O_5 on wet aerosols and chlorine-containing aerosols. Since OH radical is mainly present in the daytime while NO_3 radical and N_2O_5 are mainly present in the nocturnal atmosphere (Brown and Stutz, 2012), NO_2 + OH is usually referred as the daytime nitrate formation pathway while N_2O_5 + H_2O/Cl^- and NO_3 + HC are referred as nocturnal formation pathways (Vicars et al., 2013; Sofen et al., 2014). During haze in Beijing, the mixing ratio of daytime OH is modelled to be low (Zheng et al., 2015b; Rao et al., 2016) while relatively high mixing ratio of nocturnal N_2O_5 is observed in several studies (Wang et al., 2017a; Li et al., 2018; Wang et al., 2017b), therefore, nocturnal pathways are suggested to be most responsible for the high concentrations of atmospheric nitrate during haze (Su et al., 2017; Pathak et al., 2009; Pathak et al., 2011). In addition, the high $PM_{2.5}$ concentration and relative humidity during haze in Beijing favors heterogeneous reactions, which renders NO_2 + H_2O being a potentially significant pathway for nitrate production (Wang et al., 2017d; Tong et al., 2015; Zheng et al., 2015a).

Nitrogen isotopic composition of nitrate ($\delta^{15}N(NO_3^-)$, wherein $\delta^{15}N = (R_{sample}/R_{reference} - 1)$ with R representing isotope ratios of $^{15}N/^{14}N$ in the sample and the reference atmospheric N_2) is useful in tracing source of its precursor NO_X (Xiao et al., 2015; Beyn et al., 2014; Fang et al., 2011; Hastings et al., 2013). Anthropogenic sources of NO_X such as coal combustion are generally enriched in $\delta^{15}N$ while natural NO_X sources such as soil emissions or lighting typically have negative or zero $\delta^{15}N$ signature (Hoering, 1957; Yu and Elliott, 2017; Felix et al., 2012). Therefore highly positive values of observed $\delta^{15}N(NO_3^-)$ can be considered as an indicator of anthropogenic combustion (Elliott et al., 2009; Fang et al., 2011), although this judgment may be influenced by isotopic exchange between NO and NO_2 (Freyer et al., 1993; Walters et al., 2016), isotopic fractionations associated with nitrate formation pathways and isotopic effects occurring during transport, such as deposition of NO_3^- and HNO_3 partitioning between gas and particle phase (Freyer, 1991; Geng et al., 2014). The oxygen-17 excess ($\Delta^{17}O$) of nitrate, defined as $\Delta^{17}O = \delta^{17}O - 0.52\delta^{18}O$, wherein $\delta^{X}O = (R_{sample}/R_{reference} - 1)$ with R representing isotope ratios of $^{X}O/^{16}O$ in the sample and the reference Vienna Standard Mean Ocean Water and X = 17 or 18, is particularly useful in reflecting nitrate formation pathways (Michalski et al., 2003). Atmospheric nitrate from nocturnal reaction pathways has higher $\Delta^{17}O$ than that from daytime OH oxidation at given $\Delta^{17}O(NO_2)$ (Table 1). And once formed, atmospheric $\Delta^{17}O(NO_3^-)$ cannot be altered by mass-dependent processes such as deposition during transport (Brenninkmeijer et al., 2003). Previous studies have shown the utility of atmospheric $\Delta^{17}O(NO_3^-)$ in quantifying the relative importance of various nitrate formation pathways (Alexander et al., 2009; Michalski et al., 2003; Patris et al., 2007; Savarino et al., 2013; Vicars et al., 2013). For example, $\Delta^{17}O(NO_3^-)$-constrained box modeling work of Michalski et al. (2003) suggests that more than 90 % of atmospheric nitrate is from nocturnal $N_2O_5 + H_2O$ pathway in winter La Jolla, California, which is reflected by the highest $\Delta^{17}O(NO_3^-)$ values being observed in winter. In another study, Alexander et al. (2009) use observed $\Delta^{17}O(NO_3^-)$ to constrain 3D model and found that daytime NO_2 + OH pathway dominates global tropospheric nitrate production with an annual mean contribution of 76 %.

Until now, however, field observations of atmospheric $\Delta^{17}O(NO_3^-)$ have not been conducted in north China to constrain the relative importance of different nitrate formation pathways during haze. In this work, we present the first observations of atmospheric $\Delta^{17}O(NO_3^-)$ during Beijing haze from October 2014 to January 2015, and use this observation to examine the importance of nocturnal formation pathways. We also present the signature of simultaneously observed $\delta^{15}N(NO_3^-)$.

2 Materials and Methods

2.1 Sampling and atmospheric observations

$PM_{2.5}$ filter samples were collected at a flow rate of 1.05 m^3 min^{-1} by a high volume air sampler (model TH-1000C II, Tianhong Instruments Co., Ltd, China). The filter is quartz microfiber filter (Whatman Inc., UK), pre-combusted at 450 °C for 4 h before sampling. Our sampling period lasted from October 2014 to January 2015 with the collection interval being 12 h (08:00 – 20:00 LT or 20:00 – 08:00 LT) for each sample. Blank control samples were also collected. The blank was sampled identically to the real sample except that the collection interval is 1 min. Due to that gaseous HNO_3 is likely to adsorb onto particulate matter already trapped by the filter material (Vicars et al., 2013), the nitrate species collected is likely to include both particulate nitrate and gaseous HNO_3, which is referred to as atmospheric nitrate in previous studies (Vicars et al., 2013; Morin et al., 2009; Michalski et al., 2003) and in this study. The sampling site is at the campus of University of the Chinese Academy of Sciences (40.41 ° N, 116.68 ° E, ~20 m high) in suburban Beijing, about 60 km northeast of downtown (Fig. 2), which is a super site set by HOPE-J^{3}A (Haze Observation Project Especially for Jing-Jin-Ji Area) with various observations being reported (Zhang et al., 2017; Xu et al., 2016; Chen et al., 2015; Tong et al., 2015; He et al., 2018). Hourly concentrations of surface $PM_{2.5}$, CO, SO_2, NO_2 and O_3 were observed at Huairou station (40.33 ° N, 116.63 ° E) by Beijing Municipal Environmental Monitoring Center, about 10 km to our sampling site. Meteorological data including relative humidity (RH) and air temperature (T) were measured by an automatic weather station (model MetPak, Gill Instruments Limited, UK). Time used in the present study is local time (LT = UTC + 8).

2.2 Measurements of ions and isotopic ratios

Ion concentrations of NO_3^- and Cl^- were measured in Anhui Province Key Laboratory of Polar Environment and Global Change in the University of Science and Technology of China. A detailed description of this method can be found in the literature (Ye et al., 2015). Briefly, ions in the $PM_{2.5}$ filter sample were extracted with Millipore water (≥ 18 MΩ) and insoluble substances in the extract were filtered. Then the ion concentrations were analyzed by an ion chromatograph system (model Dionex ICS-2100, Thermo Fisher Scientific Inc., USA). The measured ion concentrations of blank samples were subtracted when determining the ion concentrations of real samples. Typical analytical precision by our method is better than 10 % relative standard deviation (RSD) (Chen et al., 2016).

$\delta^{15}N(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$ were measured with a bacterial denitrifier method (Kaiser et al., 2007) in IsoLab at the University of Washington, USA. Briefly, ions in the filter sample were extracted with Millipore water (≥ 18 MΩ) and the insoluble substances were filtered. NO_3^- in each sample was converted to N_2O by the denitrifying bacteria, Pseudomonas aureofaciens. Then N_2 and O_2, which were decomposed from N_2O in a gold tube at 800 ° C, were separated by a gas chromatograph. The isotopic ratios of each gas were then measured by a Finnigan Delta-Plus Advantage isotope ratio mass spectrometer. Masses of 28 and 29 from N_2 were measured to determine $\delta^{15}N$. Masses of 32, 33 and 34 from O_2 were measured to determine $\delta^{17}O$ and $\delta^{18}O$ and $\Delta^{17}O$ was then calculated. We use international nitrate reference materials, USGS34, USGS35 and $IAEANO_3$, for data calibration. The uncertainty (1σ) of $\delta^{15}N$ and $\Delta^{17}O$ measurements in our method is 0.4 ‰ and 0.2 ‰, respectively, based on replicate analysis of the international reference materials. All the samples including blank samples were measured in triplicate to quantify the uncertainty in each sample. The blank was subtracted for each sample by using an isotopic mass balance on the basis of isotopic ratios and concentrations of the blank. To minimize the blank effect, samples with blank concentrations being > 10 % of their concentrations were not analyzed for isotopic ratios. This ruled out 3 of the total 34 samples, all of which are in non-polluted days (NPD, $PM_{2.5} < 75$ μg m^{-3}). Totally, isotopic compositions of 7 samples in NPD and 24 samples in polluted days (PD, $PM_{2.5} \geq 75$ μg m^{-3}) are reported here.

2.3 Estimate of different nitrate formation pathways based on $\Delta^{17}O(NO_3^-)$

The observed $\Delta^{17}O(NO_3^-)$ is determined by the relative importance of different nitrate formation pathways and the relative importance of O_3 oxidation in NO_X cycling as shown in Eq. (1):

$$\Delta^{17}\mathrm{O}(\mathrm{NO_3^-}) = \Delta^{17}\mathrm{O}_{\mathrm{R6}} \times f_{\mathrm{R6}} + \Delta^{17}\mathrm{O}_{\mathrm{R7}} \times f_{\mathrm{R7}} + \Delta^{17}\mathrm{O}_{\mathrm{R8}} \times f_{\mathrm{R8}} + \Delta^{17}\mathrm{O}_{\mathrm{R9}} \times f_{\mathrm{R9}} + \Delta^{17}\mathrm{O}_{\mathrm{R10}} \times f_{\mathrm{R10}} \qquad (1)$$

Where $\Delta^{17}O_{R6}$, $\Delta^{17}O_{R7}$, $\Delta^{17}O_{R8}$, $\Delta^{17}O_{R9}$ and $\Delta^{17}O_{R10}$ is respectively $\Delta^{17}O(NO_3^-)$ resulting from $NO_2 + OH$, $NO_2 + H_2O$, $NO_3 + HC$, $N_2O_5 + H_2O$ and $N_2O_5 + Cl^-$ pathway (Table 1). f_{R6}, f_{R7}, f_{R8}, f_{R9} and f_{R10} is respectively corresponding fractional contribution of above pathways to nitrate production. By using the $\Delta^{17}O$ assumptions for different pathways in Table 1 and the definition $f_{R6} + f_{R7} + f_{R8} + f_{R9} + f_{R10} = 1$, Eq. (1) is further expressed as:

$$\Delta^{17}\mathrm{O}(\mathrm{NO_3^-})/‰ = 25\alpha f_{\mathrm{R6}} + 25\alpha f_{\mathrm{R7}} + (25\alpha + 14) \times f_{\mathrm{R8}} + (25\alpha + 7) \times f_{\mathrm{R9}} + (25\alpha + 14) \times f_{\mathrm{R10}} = 25\alpha + 14 \times (f_{\mathrm{R8}} + f_{\mathrm{R10}}) + 7 f_{\mathrm{R9}} \qquad (2)$$

Where α is the proportion of O_3 oxidation in NO_2 production rate, calculated by Eq. (3):

$$\alpha = \frac{k_{\mathrm{R1}}[\mathrm{NO}][\mathrm{O_3}]}{k_{\mathrm{R1}}[\mathrm{NO}][\mathrm{O_3}] + k_{\mathrm{R2a}}[\mathrm{NO}][\mathrm{HO_2}] + k_{\mathrm{R2b}}[\mathrm{NO}][\mathrm{RO_2}]} \quad (3)$$

In Eq. (3), k_{R1}, k_{R2a} and k_{R2b} is respectively the reaction rate constant listed in Table 2. To evaluate α, we estimated HO_2 mixing ratios on the basis of empirical formulas between HO_2 and O_3 mixing ratios derived from observations in winter (Kanaya et al., 2007), that's: $[\mathrm{HO_2}]/(\mathrm{pmol\ mol^{-1}}) = \exp(5.7747 \times 10^{-2} \times [\mathrm{O_3}]/(\mathrm{nmol\ mol^{-1}}) - 1.7227)$ during the day time and $[\mathrm{HO_2}]/(\mathrm{pmol\ mol^{-1}}) = \exp(7.7234 \times 10^{-2} \times [\mathrm{O_3}]/(\mathrm{nmol\ mol^{-1}}) - 1.6363)$ at night. Then RO_2 mixing ratio was calculated as 70 % of HO_2 mixing ratios based on previous studies (Liu et al., 2012; Elshorbany et al., 2012; Mihelcic et al., 2003). As NO mixing ratio was not observed in our study, we estimated NO mixing ratios following the empirical formulas between NO_X and CO mixing ratios derived from observations in winter Beijing (Lin et al., 2011), that's: $[\mathrm{NO}]/(\mathrm{nmol\ mol^{-1}}) = ([\mathrm{CO}]/(\mathrm{nmol\ mol^{-1}}) - 196)/27.3 - [\mathrm{NO_2}]/(\mathrm{nmol\ mol^{-1}})$ during daytime and $[\mathrm{NO}]/(\mathrm{nmol\ mol^{-1}}) = ([\mathrm{CO}]/(\mathrm{nmol\ mol^{-1}}) - 105)/30.9 - [\mathrm{NO_2}]/(\mathrm{nmol\ mol^{-1}})$ at night.

By using Eq. (2), the relative importance of nocturnal formation pathways ($f_{\mathrm{R8}} + f_{\mathrm{R9}} + f_{\mathrm{R10}}$) can be written as Eq. (4):

$$f_{\mathrm{R8}} + f_{\mathrm{R9}} + f_{\mathrm{R10}} = \frac{f_{\mathrm{R9}}}{2} + \frac{\Delta^{17}\mathrm{O(NO_3^-)}}{14‰} - 1.8\alpha \quad (4)$$

Eq. (4) suggests that the relative importance of nocturnal pathways is solely a function of the assumption of f_{R9} at given $\Delta^{17}\mathrm{O(NO_3^-)}$ and α. Since f_{R9}, $f_{\mathrm{R8}} + f_{\mathrm{R10}}$ and $f_{\mathrm{R8}} + f_{\mathrm{R9}} + f_{\mathrm{R10}}$ should be in the range of 0 – 1 all the time, f_{R9} is further limited to meet Eq. (5):

$$f_{\mathrm{R9}} \begin{cases} > 0 \\ < \min\left(1, \frac{\Delta^{17}\mathrm{O(NO_3^-)}}{7‰} - 3.6\alpha, 2 + 3.6\alpha - \frac{\Delta^{17}\mathrm{O(NO_3^-)}}{7‰}\right) \end{cases} \quad (5)$$

We estimated the relative importance of nocturnal pathways ($f_{\mathrm{R8}} + f_{\mathrm{R9}} + f_{\mathrm{R10}}$) by using concentration-weighted $\Delta^{17}\mathrm{O(NO_3^-)}$ observations and production rate weighted α in PD of each haze event rather than each sample due to the lifetime of atmospheric nitrate is typically on the order of day (Liang et al., 1998), larger than our sampling collection interval.

2.4 Simulation of surface N_2O_5 and NO_3 radical

To see whether the relative importance of nocturnal pathways constrained by $\Delta^{17}\mathrm{O(NO_3^-)}$ can be reproduced by models, we use the standard Master Chemical Mechanism (MCM, version 3.3, http://mcm.leeds.ac.uk/) to simulate the mixing ratios of surface N_2O_5 and NO_3 radical during our sampling period. The input for this modeling work includes: (i) 1 h-averaged mixing ratios of observed surface CO, NO_2, SO_2 and O_3 and estimated NO (see Sect. 2.3), (ii) observed RH and *T*, and (iii) the mixing ratios of organic compounds from the literatures (Table S1) (Wang et al., 2001; Wu et al., 2016; Rao et al., 2016).

3 Results and Discussion

3.1 Overview of observations in Beijing haze

Figure 3 describes general characteristics of haze events during our observations. The 12h-averaged $PM_{2.5}$ concentrations, corresponding with filter samples, varied from 16 to 323 μg m^{-3} with a mean of (141±88 (1SD)) μg m^{-3}. In comparison, the Grade II of NAAQS (National Ambient Air Quality Standard) in China is 75 μg m^{-3} for daily $PM_{2.5}$. The NO_3^- concentrations present similar trends with $PM_{2.5}$ levels (Fig. 3a), ranged from 0.3 to 106.7 μg m^{-3} with a mean of (6.1±5.3) μg m^{-3} in non-polluted days (NPD, $PM_{2.5} < 75$ μg m^{-3}) and (48.4±24.7) μg m^{-3} in polluted days (PD, $PM_{2.5} \geq 75$ μg m^{-3}). Correspondingly, the nitrogen oxidation ratio (NOR, which equals to NO_3^- molar concentration divided by the sum of NO_3^- and NO_2 molar concentration), a proxy for secondary transformation of nitrate (Sun et al., 2006), increased from a mean of 0.09±0.05 in NPD to 0.31±0.10 in PD (Fig. 3b). In residential heating season (Case III – V in November 2014 – January 2015, Fig. 3b), Cl^- concentrations present similar trends with NO_3^- levels, increased from (0.6±1.0) μg m^{-3} in NPD to (7.9±4.8) μg m^{-3} in PD. However, during Case I – II in October 2014, Cl^- concentrations were (3.5±1.6) μg m^{-3} in NPD and (3.5±1.9) μg m^{-3} in PD, showing no significant difference at 0.01 level (t-test). Throughout our observational period, the visibility decreased from (11.4±6.7) km in NPD to (3.1±1.8) km in PD (Fig. 3c) while relative humidity (RH) increased from (37±12) % in NPD to (62±12) % in PD (Fig. 3d).

$\Delta^{17}O(NO_3^-)$ ranged from 27.5 ‰ to 33.9 ‰ with the mean of (29.1±1.3) ‰ in NPD and (31.0±1.7) ‰ in PD (Fig. 3c). Our observed $\Delta^{17}O(NO_3^-)$ is in the range of aerosol $\Delta^{17}O(NO_3^-)$ reported in literatures (Table 3) and similar to wet deposition $\Delta^{17}O(NO_3^-)$ observed in East Asia (Nelson et al., 2018; Tsunogai et al., 2016; Tsunogai et al., 2010). All our observed $\Delta^{17}O(NO_3^-)$ values, no matter daytime sample (08:00 – 20:00) or nighttime sample (20:00 – 08:00), are larger than 25 ‰, the maximum of $\Delta^{17}O(NO_3^-)$ that can be produced via $NO_2 + OH$ and $NO_2 + H_2O$ (Table 1) at the assumption of bulk $\Delta^{17}O(O_3)$ = 26 ‰ (Ishino et al., 2017; Vicars and Savarino, 2014). This directly suggests nocturnal formation pathways ($N_2O_5 + H_2O/Cl^-$ and NO_3 + HC) must contribute to all the sampled nitrate. Given the lifetime of atmospheric nitrate is typically larger than our sampling collection interval (Vicars et al., 2013), each of our samples is expected to reflect both daytime and nocturnal nitrate production. Not surprisingly, $\Delta^{17}O(NO_3^-)$ mean of daytime and nighttime samples is (30.3±1.5) ‰ and (30.9±2.1) ‰, respectively, showing no significant difference at 0.01 level (t-test).

$\delta^{15}N(NO_3^-)$ in our observation varied from –2.5 ‰ to 19.2 ‰ with a mean of (7.4±6.8) ‰, which is in the range of $\delta^{15}N(NO_3^-)$ observed from rainwater in Beijing, China (Zhang et al., 2008) and similar to $\delta^{15}N(NO_3^-)$ values observed from aerosols in Germany (Freyer, 1991). Figure 3d shows that $\delta^{15}N(NO_3^-)$ varies largely in October 2014. The mean $\delta^{15}N(NO_3^-)$ varied from (0.4±1.5) ‰ in 08:00 Oct. 18 – 08:00 Oct. 21 to (10.7±1.4) ‰ in 08:00 Oct. 21 – 08:00 Oct. 23 and then decreased to (–0.9±2.1) ‰ in 08:00 Oct. 23 – 08:00 Oct. 26, which corresponds to $PM_{2.5}$ concentrations being 155±63, 57±19 and (188±51) μg m^{-3} respectively. However, during residential heating season, relatively high $\delta^{15}N(NO_3^-)$ (7.6 – 19.2 ‰) were always observed both in NPD and PD. This may be related to the high NO_X emission from coal combustion in north China (Wang et al., 2012; Lin, 2012; Zhang et al., 2007).

3.2 Relationships between $\Delta^{17}O(NO_3^-)$ and other data

Figure 4 presents the relationships between $\Delta^{17}O(NO_3^-)$ and NO_3^- concentrations, $PM_{2.5}$ concentrations, NOR, visibility, RH and $\delta^{15}N(NO_3^-)$. $\Delta^{17}O(NO_3^-)$ shows a positive correlation with NO_3^- concentrations when $NO_3^- < 50$ μg m^{-3} (r = 0.81, p < 0.01). Similarly, $\Delta^{17}O(NO_3^-)$ shows a positive correlation with $PM_{2.5}$ concentration in Fig. 4b and NOR in Fig. 4c when $NO_3^- < 50$ μg m^{-3} (r = 0.71 and r = 0.80, p < 0.01, respectively). Figure 4d shows that $\Delta^{17}O(NO_3^-)$ is negative correlated with visibility in general (r = –0.66, p < 0.01). The significant decrease of visibility will largely reduce surface radiation and thereby OH mixing ratios (Zheng et al., 2015b), which is unfavorable for nitrate production via NO_2 + OH pathway. Since NO_2 + OH pathway produces low $\Delta^{17}O(NO_3^-)$ (Table 1), the decreased importance of NO_2 + OH pathway will conversely increase $\Delta^{17}O(NO_3^-)$. While the raise of RH accompanying the large increase of $PM_{2.5}$ favors nitrate production via heterogeneous uptake of gases, e.g., N_2O_5 (Zheng et al., 2015b; Zheng et al., 2015a) and heterogeneous uptake of N_2O_5 produces relative high $\Delta^{17}O(NO_3^-)$ (Table 1), the enhanced heterogeneous uptake of N_2O_5 will increase $\Delta^{17}O(NO_3^-)$ too. Therefore, the decrease of importance of NO_2 + OH and the increase of importance of heterogeneous uptake of N_2O_5 should be responsible for the positive correlation between $\Delta^{17}O(NO_3^-)$ and NO_3^- concentrations. In addition, for samples with $NO_3^- >$ 50 μg m^{-3}, visibility was always low with narrow variations (2.3±1.0 km) and RH was always high with narrow range (67±7 %), which may be responsible for the relatively high $\Delta^{17}O(NO_3^-)$ being observed (31.2±1.7 ‰). Figure 4f shows that $\Delta^{17}O(NO_3^-)$ is not correlated with $\delta^{15}N(NO_3^-)$.

3.3 Estimate of nocturnal formation pathways

Before estimating the relative importance of different nitrate formation pathways, we estimate the proportion of O_3 oxidation in NO_2 production rate, α. The possible α range can be calculated based on observed $\Delta^{17}O(NO_3^-)$. It can be obtained from Table 1 that 25α ‰ $< \Delta^{17}O(NO_3^-) < (25\alpha + 14)$ ‰, so the lower limit of possible α is $(\Delta^{17}O(NO_3^-) - 14$ ‰$)/25$ ‰. And since $\Delta^{17}O(NO_3^-) \geq 27.5$ ‰ in our observation, the higher limit of α is always 1 for all the samples. Figure 5 presents the possible range of calculated α based on $\Delta^{17}O(NO_3^-)$. The calculated lower limit of α ranged from 0.56 to 0.81 with a mean of 0.68±0.07, which directly suggests that O_3 oxidation played a dominated role in NO_X cycling during Beijing haze. To estimate the specific α value, chemical kinetics in Table 2 and Eq. (3) were used. Specific α is estimated to range from 0.86 to 0.97 with a mean of (0.94±0.03), which is in the possible range of α value calculated directly based on $\Delta^{17}O(NO_3^-)$ (Fig. 5) and close to the range of 0.85 – 1 determined in other mid-latitude areas (Michalski et al., 2003; Patris et al., 2007).

Figure 6a shows the estimated relative importance of nocturnal formation pathways (N_2O_5 + H_2O/Cl^- and NO_3 + HC) during PD of each case on the basis of observed $\Delta^{17}O(NO_3^-)$. Possible fractional contribution of nocturnal formation pathways ranges from 49 – 97 %, 58 – 100 %, 60 – 100 %, 45 – 90 % and 70 – 100 % in PD of Case I to V, respectively, with a mean of 56 – 97 %. This directly implies that nocturnal chemistry dominates atmospheric nitrate production in Beijing haze. This finding is consistent with the suggested importance of heterogeneous uptake of N_2O_5 during Beijing haze by previous studies (Su et al., 2017; Wang et al., 2017b). The other pathways (NO_2 + OH and NO_2 + H_2O) account for the remaining fraction with a mean possible range of 3 – 44 %. Since NO_2 + OH and NO_2 + H_2O produces the same $\Delta^{17}O(NO_3^-)$ signature in our assumptions (Table 1), we cannot distinguish their fractional contribution barely from the observed $\Delta^{17}O(NO_3^-)$ in the present study. However, the overall positive correlation between $\Delta^{17}O(NO_3^-)$ and RH ($r = 0.55$, $p < 0.01$, Fig. 4e) suggests heterogeneous uptake of NO_2 should be less important than heterogeneous uptake of N_2O_5, otherwise, a negative relationship between $\Delta^{17}O(NO_3^-)$ and RH is expected. Our calculations also suggest that the sum of possible fractional contribution of N_2O_5 + Cl^- and NO_3 + HC is in the range of 0 – 49 %, 17 – 58 %, 20 – 60 %, 0 – 45 % and 41 – 70 % in PD of Case I to V, respectively, with a mean of 16 – 56 % (Table 4), which emphasizes that N_2O_5 + Cl^- and NO_3 + HC played a non-ignorable role in nitrate production during Beijing haze. Due to that N_2O_5 + Cl^- and NO_3 + HC produce the same $\Delta^{17}O(NO_3^-)$ in our assumptions (Table 1), we cannot distinguish their fractional contribution barely from the observed $\Delta^{17}O(NO_3^-)$ in this study, either. However, NO_3 + HC should be minor for nitrate production. For example, 3D modelling work of Alexander et al. (2009) suggests NO_3 + HC pathway only accounts for 4 % of global tropospheric nitrate production annually on average, and Michalski et al. (2003) found that NO_3 + HC pathway contributes 1 – 10 % to nitrate production on the basis of an annual observation at La Jolla, California, with low values in winter. Therefore, in addition to NO_3 + HC, N_2O_5 + Cl^- is likely to also contribute to nitrate production during haze in Beijing. Supportively, the concentrations of Cl^- is as high as (5.5±4.1) $\mu g\ m^{-3}$ during PD of all the cases in our observation and the mixing ratios of $ClNO_2$, an indicator of N_2O_5 + Cl^- pathway, reached up to 2.9 nmol mol^{-1} during a summer observation in suburban Beijing (Wang et al., 2018b) and reached up to 5.0 nmol mol^{-1} in a modelling work in summer rural Beijing (Wang et al., 2017c).

Figure 6b presents the simulated mixing ratios of surface N_2O_5 and NO_3 radical during our observational period by using the box model MCM. The 12h averaged mixing ratios of simulated N_2O_5 ranged from 3 to 649 pmol mol^{-1} while simulated NO_3 radical ranged from 0 to 27 pmol mol^{-1}. In comparison, previous observations in Beijing suggest 5s averaged N_2O_5 can be as high as 1.3 nmol mol^{-1} and 30 min averaged NO_3 radical can be as high as 38 pmol mol^{-1} with large day-to-day variability (Wang et al., 2017b; Wang et al., 2015). During Case I and II in October, simulated N_2O_5 and NO_3 radical present similar trends with the observed NO_3^- and remain relatively high during PD (346±128 pmol mol^{-1} and 9±7 pmol mol^{-1}, respectively, Fig. 6b), which supports the dominant role of nocturnal formation pathways suggested by $\Delta^{17}O(NO_3^-)$. However, during Case III – V in residential heating season, the simulated surface mixing ratios of N_2O_5 and

NO_3 radical remain relatively low during PD (63±80 pmol mol^{-1} and < 1 pmol mol^{-1}, respectively, Fig. 6b), which seems to be inconsistent with $\Delta^{17}O(NO_3^-)$ observations. We note that a recent study suggests that heterogeneous uptake of N_2O_5 is negligible at surface but larger at higher altitudes (e.g., > 150 m) during winter haze in Beijing (Wang et al., 2018a). So during PD of Case III – V in our observational period, large nitrate production via heterogeneous uptake of N_2O_5 may occur aloft rather than at surface, which leads to the dominant role of nocturnal formation pathways as suggested by $\Delta^{17}O(NO_3^-)$.

4 Conclusions

We report the first observation of isotopic composition ($\Delta^{17}O$ and $\delta^{15}N$) of atmospheric nitrate in Beijing haze. The observed $\Delta^{17}O(NO_3^-)$ ranged from 27.5 ‰ to 33.9 ‰ with a mean of (30.6±1.8) ‰. $\delta^{15}N(NO_3^-)$ ranged largely from –2.5 ‰ to 19.2 ‰ with a mean of (7.4±6.8) ‰. When NO_3^- is < 50 μg m^{-3}, a positive correlation was observed between $\Delta^{17}O(NO_3^-)$ and NO_3^- concentration ($r = 0.81$, $p < 0.01$). This is likely to result from the variation of relative importance of different nitrate formation pathway. Calculations with the constraint of $\Delta^{17}O(NO_3^-)$ suggest that nocturnal pathways ($N_2O_5 + H_2O/Cl^-$ and NO_3 + HC) dominated nitrate production during polluted days ($PM_{2.5} \geq 75$ μg m^{-3}), with the mean possible contribution of 56 – 97 %. $\Delta^{17}O(NO_3^-)$ also indicates that O_3 dominated NO oxidation during Beijing haze.

Supplementary Materials

Figure S1. The diurnal differences of observed NO_2, CO and O_3 and calculated NO, HO_2 and RO_2 during our sampling periods.

Table S1. The input of organic compounds for MCM model (nmol mol^{-1}).

Data availability

All data needed to draw the conclusions are present in the main text and/or the Supplementary Materials. For additional data, please contact the corresponding author (zqxie@ustc.edu.cn).

Author contributions

Z.Q.X. conceived this study. P.Z.H. conducted isotope measurements. P.Z.H., X.Y.C, S.D.F., H.C.Z., H. K. performed the field experiments and ion measurements. P.Z.H., Z.Q.X., X.W.Y. interpreted the data. C.L. contributed to the field observation support. P.Z.H. wrote the manuscript with Z.Q.X. inputs. All authors involved the discussion and revision.

Competing interests

The authors declare no competing interests.

Acknowledgments

This work was supported by the National Key Project of MOST (2016YFC0203302), NSFC (91544013), the Key Project of CAS (KJZD-EW-TZ-G06-01) and the Atmospheric Pollution Control of the Prime Minister (DQGG0104). We gratefully thank staffs of IsoLab at UW for their technical support, Becky Alexander and Lei Geng for helpful discussions.

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Figures and Tables

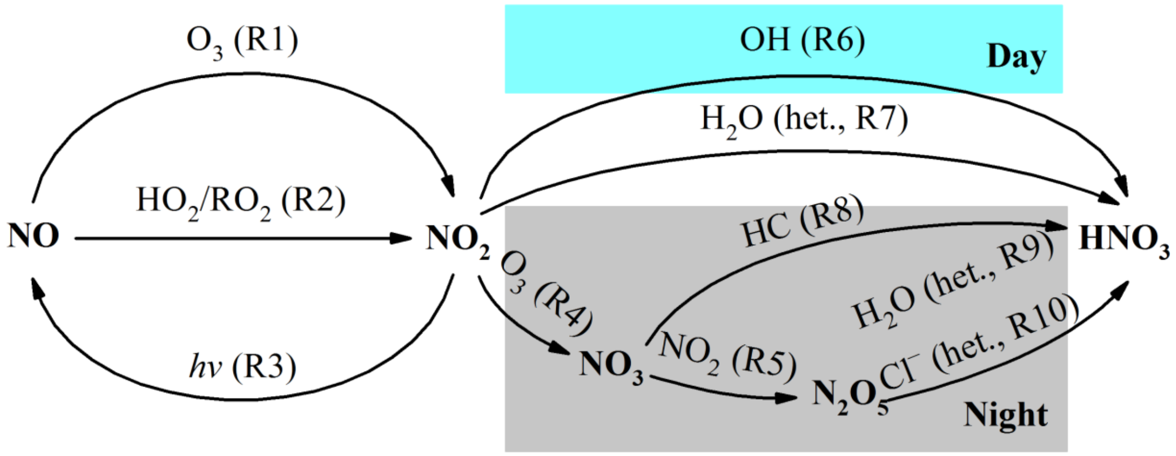

Figure 1. Simplified schematic of the main nitrate formation pathways in urban air. "het." means heterogeneous reactions on aerosols.

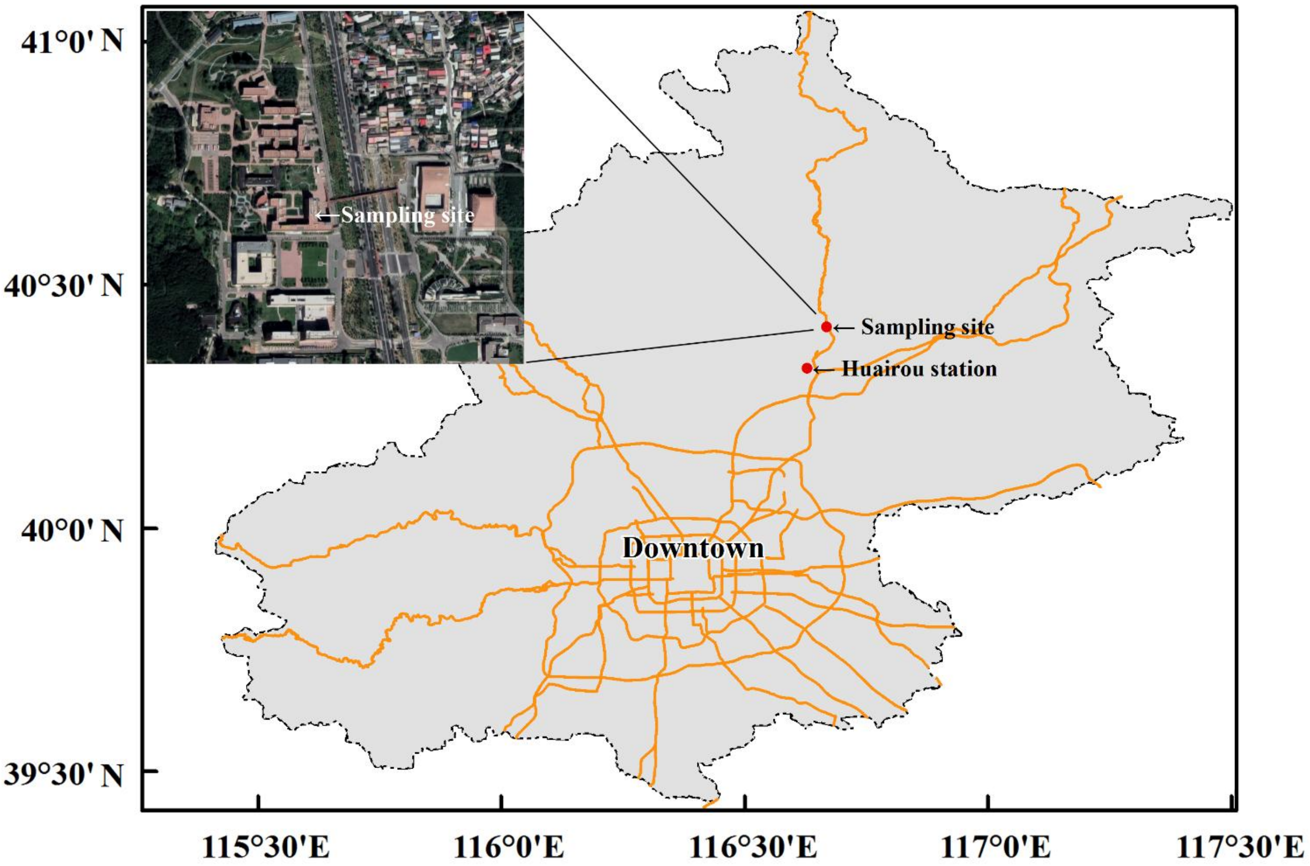

Figure 2. A brief map of sampling site in Beijing. The map scale of base map is 1:1250000. Huairou station is set by Beijing Municipal Environmental Monitoring Center, where hourly $PM_{2.5}$, SO_2, CO, NO_2 and O_3 were observed.

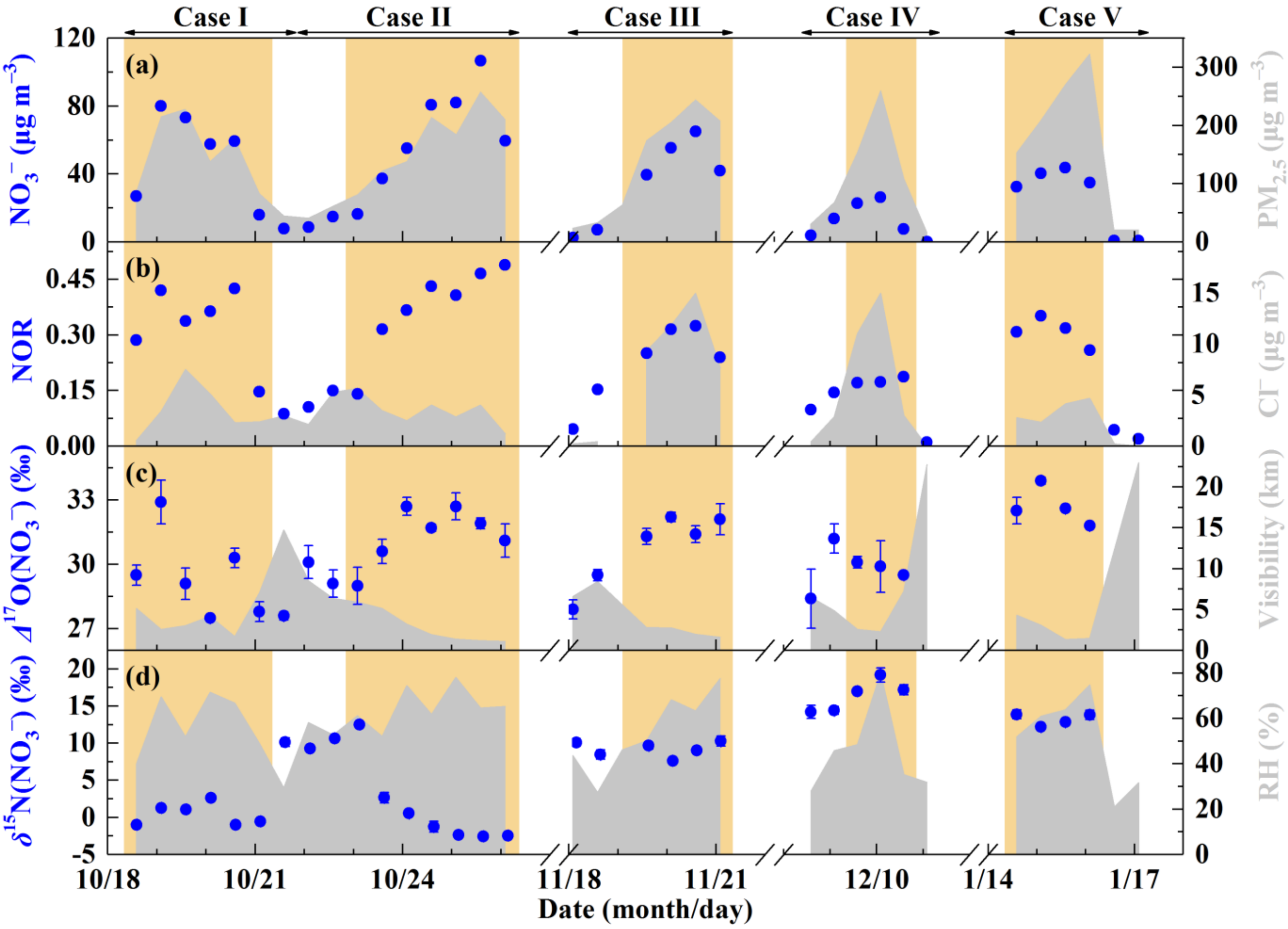

Figure 3. General characteristics of haze events in Beijing (October 2014 – January 2015). **(a)** Time series of $PM_{2.5}$ and NO_3^- concentrations. **(b)** Time series of nitrogen oxidation ratio (NOR, which equals to NO_3^- molar concentration divided by the sum of NO_3^- and NO_2 molar concentration) and Cl^- concentrations. **(c)** Time series of $\Delta^{17}O(NO_3^-)$ and visibility. **(d)** Time series of $\delta^{15}N(NO_3^-)$ and relative humidity (RH). The error bars in (c) and (d) are ±1σ of replicate measurements (n = 3) of each sample. The khaki shaded area indicates polluted days (PD, $PM_{2.5} \geq 75$ μg m^{-3}).

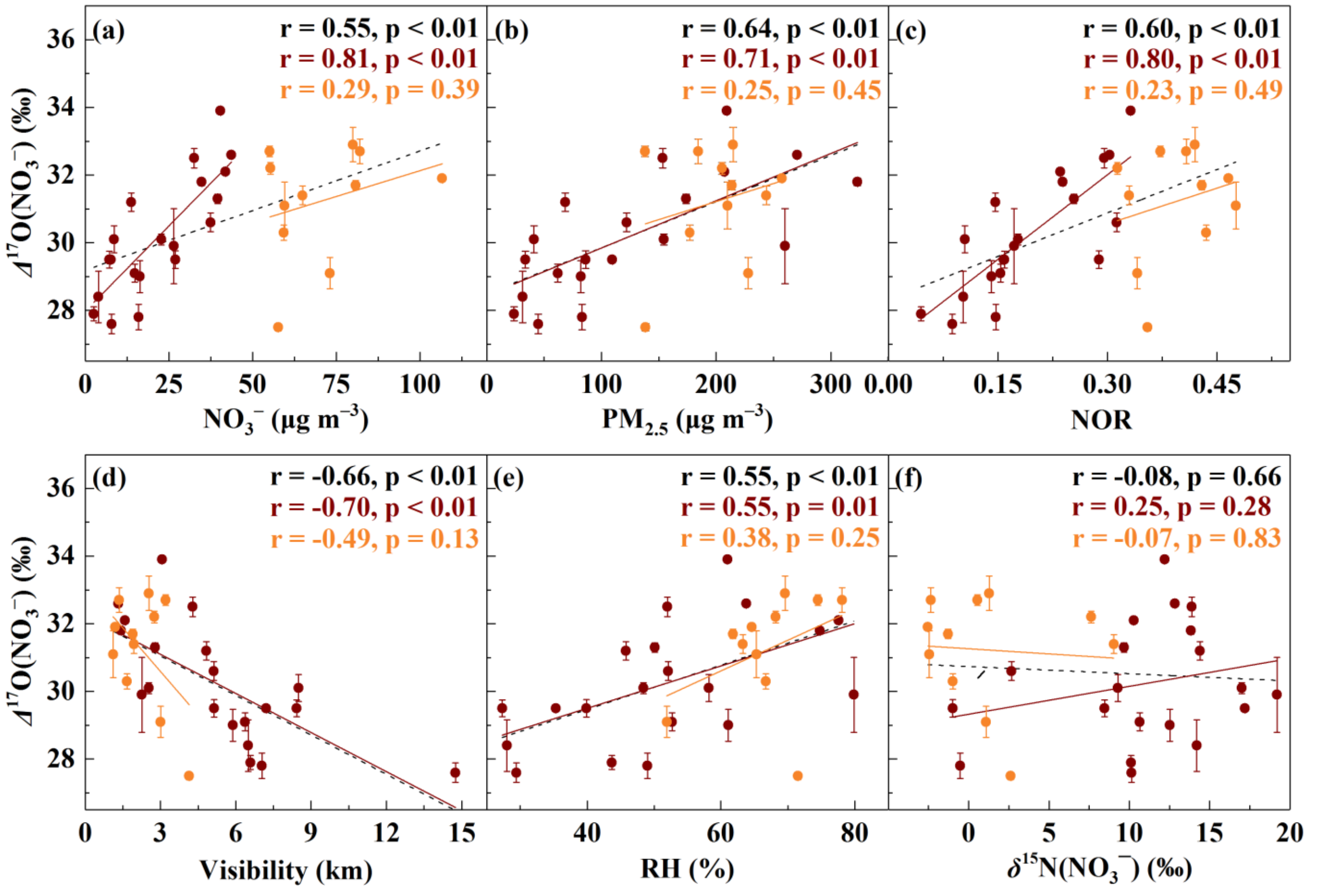

Figure 4. Relationships between $\Delta^{17}O(NO_3^-)$ and other parameters. The relationship between $\Delta^{17}O(NO_3^-)$ and NO_3^- concentrations (**a**), $PM_{2.5}$ concentrations (**b**), nitrogen oxidation ratio (NOR, **c**), visibility (**d**), relative humidity (RH, **e**) and $\delta^{15}N(NO_3^-)$ (**f**). The dark red dots are samples with $NO_3^- < 50\ \mu g\ m^{-3}$ and the orange dots are samples with $NO_3^- > 50\ \mu g\ m^{-3}$. The black dash lines are linear least-squares fitting lines for all samples, the dark red solid lines are linear least-squares fitting lines for samples with $NO_3^- < 50\ \mu g\ m^{-3}$ and the orange solid lines are linear least-squares fitting lines for samples with $NO_3^- > 50\ \mu g\ m^{-3}$. The error bars are ±1σ of replicate measurements of each sample.

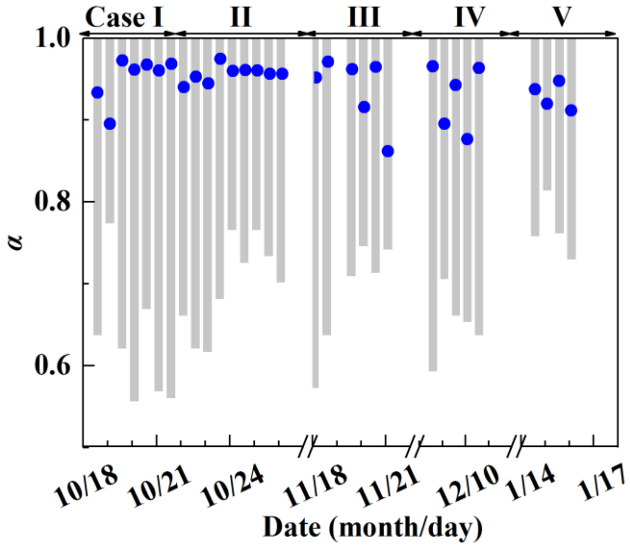

Figure 5. Estimate of the proportion of O_3 oxidation in NO_X cycling, α. The gray column represents possible α range

determined by $\Delta^{17}O(NO_3^-)$. The blue dot represents specific α value calculated by Eq. (3).

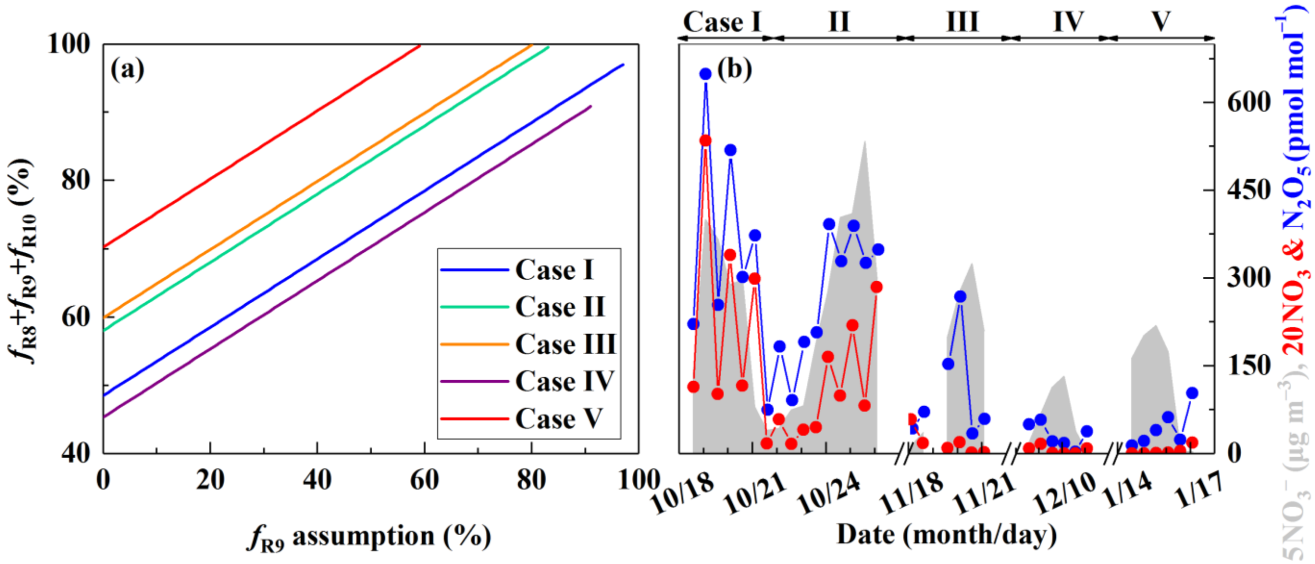

Figure 6. Estimate of the nocturnal formation pathways. The estimated relative importance of nocturnal formation pathways (f_{R8} + f_{R9} + f_{R10}) during PD of each case on the basis of observed $\Delta^{17}O(NO_3^-)$ (See Sect. 2.3, **a**) and the simulated mixing ratios of N_2O_5 and NO_3 radical by MCM (**b**). R8, R9 and R10 in (a) represents NO_3 + HC, N_2O_5 + H_2O and N_2O_5 + Cl^- pathway, respectively.

Table 1. Isotope assumptions of different nitrate formation pathways.

No.	Reaction	$\Delta^{17}O$ of product		Reference
		Expression	Value (‰) [a]	
R1	$NO + O_3 \rightarrow NO_2 + O_2$	$\Delta^{17}O(NO_2) = 1.18\times\Delta^{17}O(O_3) + 6.6$ ‰	37	(Savarino et al., 2008)
R2	$NO + HO_2/RO_2 \rightarrow NO_2 + OH/RO$	$\Delta^{17}O(NO_2) = 0.0$	0.0	(Sofen et al., 2014)
R4	$NO_2 + O_3 \rightarrow NO_3 + O_2$	$\Delta^{17}O(NO_3) = \frac{2}{3}\Delta^{17}O(NO_2) + \frac{1}{3}(1.23\times\Delta^{17}O(O_3) + 9.0$ ‰$)$	25α + 14	(Berhanu et al., 2012)
R5	$NO_2 + NO_3 \rightarrow N_2O_5$	$\Delta^{17}O(N_2O_5) = \frac{2}{5}\Delta^{17}O(NO_2) + \frac{3}{5}\Delta^{17}O(NO_3)$	30α + 8	(Sofen et al., 2014)
R6	$NO_2 + OH \rightarrow HNO_3$	$\Delta^{17}O(NO_3^-) = \frac{2}{3}\Delta^{17}O(NO_2)$	25α	(Sofen et al., 2014)
R7	$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$	$\Delta^{17}O(NO_3^-) = \frac{2}{3}\Delta^{17}O(NO_2)$	25α	[b]
R8	$NO_3 + HC \rightarrow HNO_3$ + products	$\Delta^{17}O(NO_3^-) = \Delta^{17}O(NO_3)$	25α + 14	(Sofen et al., 2014)
R9	$N_2O_5 + H_2O \rightarrow 2HNO_3$	$\Delta^{17}O(NO_3^-) = \frac{5}{6}\Delta^{17}O(N_2O_5)$	25α + 7	(Sofen et al., 2014)
R10	$N_2O_5 + Cl^- \rightarrow HNO_3 + ClNO_2$	$\Delta^{17}O(NO_3^-) = \Delta^{17}O(NO_3)$	25α + 14	[c]

[a] The values are calculated on assumptions that bulk $\Delta^{17}O(O_3)$ = 26 ‰ (Vicars and Savarino, 2014; Ishino et al., 2017) and $\Delta^{17}O(HO_2/RO_2)$ = 0 ‰. $\Delta^{17}O(RO_2)$ is equal to 0 ‰ in the troposphere (Morin et al., 2011), in contrast, observations suggest $\Delta^{17}O(HO_2)$ = 1 – 2 ‰ (Savarino and Thiemens, 1999). However, the difference in calculated $\Delta^{17}O(NO_3^-)$ between assuming

$\Delta^{17}O(HO_2)$ = 0 ‰ and $\Delta^{17}O(HO_2)$ = 2 ‰ is negligible in this study (< 0.1 ‰). And the assumption that $\Delta^{17}O(HO_2)$ = 0 ‰ simplifies calculations and is also consistent with previous studies (Michalski et al., 2003; Alexander et al., 2009; Morin et al., 2008; Kunasek et al., 2008; Sofen et al., 2014). α is the proportion of O_3 oxidation in NO_2 production rate, calculated by Eq. (3).

[b] Previous studies suggest that in R7 one oxygen atom of NO_3^- is from H_2O and the other two are from NO_2 (Li et al., 2010; Cheung et al., 2000; Goodman et al., 1999), which will result in $\Delta^{17}O(NO_3^-) = 2/3\Delta^{17}O(NO_2)$.

[c] R4 and R5 suggest that the central oxygen atom of N_2O_5 ($O_2N\text{-}O\text{-}NO_2$) is from NO_3 radical ($O\text{-}NO_2$) with $\Delta^{17}O$ (‰) = $1.23\times\Delta^{17}O(O_3)$ + 9.0 ‰. R10 is suggested to occur via $O_2N\text{-}O\text{-}NO_2\ (aq) \leftrightarrow NO_2^+ + NO_3^-$ and the following $NO_2^+ + Cl^- \rightarrow ClNO_2$ (Bertram and Thornton, 2009), so $\Delta^{17}O(NO_3^-) = 1/3(1.23\times\Delta^{17}O(O_3) + 9.0\text{ ‰}) + 2/3\Delta^{17}O(NO_2) = \Delta^{17}O(NO_3)$.

Table 2. Reaction expressions for different NO_2 production pathways.

No.	Reaction	Rate expression	Rate constant (cm^3 $molecule^{-1}$ s^{-1})	Reference
R1	$NO + O_3 \rightarrow NO_2 + O_2$	$k_{R1}[NO][O_3]$	$k_{R1}=3.0\times10^{-12}\times e^{(-1500/T)}$	(Burkholder et al., 2015)
R2a	$NO + HO_2 \rightarrow NO_2 + OH$	$k_{2Ra}[NO][HO_2]$	$k_{2Ra}=3.3\times10^{-12}\times e^{(270/T)}$	(Burkholder et al., 2015)
R2b	$NO + RO_2 \rightarrow NO_2 + RO$	$k_{2Rb}[NO][RO_2]$	$k_{2Rb} = k_{2Ra}$	(Burkholder et al., 2015; Kunasek et al., 2008)

Table 3. Atmospheric $\Delta^{17}O(NO_3^-)$ in aerosols obtained from the literature and this study.

Sample location	Sample period	Collection interval	$\Delta^{17}O$ (‰) range	Reference
Huairou, Beijing (40.41 °N, 116.68 °E)	October 2014 – January 2015	12 h	27.5 – 33.9 (30.6 ± 1.8)	This study
Trinidad Head, California (41.0 °N, 124.2 °W)	April – May 2002	1 – 4 days	20.1 – 27.5	(Patris et al., 2007)
La Jolla, California (32.7 °N, 117.2 °W)	March 1997 – April 1998	3 days	20 – 30.8	(Michalski et al., 2003)
Mt. Lulin, Taiwan (23.5 °N, 120.9 °E)	January – December 2010	1 day	2.7 – 31.4 (17 ± 7)	(Guha et al., 2017)
Cape Verde Island (16.9 °N, 24.9 °W)	July 2007 – May 2008	2 – 3 days	25.5 – 31.3	(Savarino et al., 2013)
Cruise in costal California (32.8 °N – 38.6 °N)	May – June 2010	2 – 22 h	19.0 – 29.2 (24.1 ± 2.2)	(Vicars et al., 2013)
Cruise from 65 °S to 79 °N	September – October 2006	1 – 4 days	Non-polar:	(Morin et al., 2009)

	April – May 2007		24 – 33	
	February – April 2006		Polar: 35 ± 2	
Alert, Nunavut (82.5 °N, 62.3 °W)	March – May 2004	3 – 4 days	29 – 35 (32.7 ± 1.8)	(Morin et al., 2007b)
Barrow, Alaska (71.3 °N, 156.9 °W)	March 2005	1 day	26 – 36	(Morin et al., 2007a)
Dumont d’Urville, Antarctic (66.7 °S, 140.0 °E)	January – December 2001	10 – 15 days	20.0 – 43.1	(Savarino et al., 2007)
Dumont d’Urville, Antarctic (66.7 °S, 140.0 °E)	January 2011 – January 2012	7 days	23.0 – 41.9	(Ishino et al., 2017)

Table 4 The possible range of fractional contribution of different nitrate formation pathways during PD of each case estimated on the basis of observed $\Delta^{17}O(NO_3^-)$ [a].

PD of Case	f_{R9} assumption (%)	$f_{R8} + f_{R9} + f_{R10}$ (%)	$f_{R8} + f_{R10}$ (%)	$f_{R6} + f_{R7}$ (%)
I	0 – 97	49 – 97	0 – 49	3 – 51
II	0 – 83	58 – 100	17 – 58	0 – 42
III	0 – 80	60 – 100	20 – 60	0 – 40
IV	0 – 90	45 – 90	0 – 45	10 – 55
V	0 – 59	70 – 100	41 – 70	0 – 30
Average	0 – 82	56 – 97	16 – 56	3 – 44

[a] R6, R7, R8, R9 and R10 is respectively NO_2 + OH, NO_2 + H_2O, NO_3 + HC, N_2O_5 + H_2O and N_2O_5 + Cl^- pathway.