Referee #1:

Comments: In this study, the authors investigated the formation pathways of nitrate based on $\Delta^{17}$O(NO$_3^-$) and $\delta^{15}$N(NO$_3^-$). The authors concluded that nocturnal pathways (N$_2$O$_5$ + H$_2$O and NO$_3^-$ radical + hydrocarbon) dominated the nitrate production during polluted days. Measuring the isotopic composition is an important, but underutilized approach to reveal the sources and formation pathways of atmospheric species. This study brings new insights into the nitrate sources during polluted days in Beijing. Overall, the interpretation of results is sound. However, there is room for improving the discussions. While I suggest publication after major revision, I hope that the authors will consider the following comments to make the manuscript more readable and hopefully more impactful.

A: Thanks very much for your comments. We reply to your comments one by one as follows. One point needs to be addressed here is that we have removed section 3.4 from the manuscript due to that we are unable to explain the variations of $\delta^{15}$N(NO$_3^-$) well so far.

Major Comments

1. “Nitrate” is not clearly defined in the manuscript. Based on reactions in Table 1, “nitrate” refers to HNO$_3$. However, in method section, filter-extracted NO$_3^-$ ion is analyzed. Is the implicit assumption that there is no isotope fractionation from HNO$_3$ to NO$_3^-$? Please clarify. In the literature, “nitrate” sometimes includes both inorganic nitrate (e.g., NH$_4$NO$_3$) and organic nitrate (e.g., isoprene hydroxyl nitrate). Please clarify if organic nitrate is included in the analysis of this study? In other words, can organic nitrate be analyzed by the bacterial denitrifier method?

A: Thanks for your comments. In this manuscript, atmospheric nitrate is defined as gas-phase HNO$_3$ plus particulate NO$_3^-$, which is the filter-extracted NO$_3^-$ ion analyzed by ion chromatography and is consistent with previous studies (e.g., (Vicars et al., 2013; Morin et al., 2009; Michalski et al., 2003; Alexander et al., 2009)). Once formed, the oxygen-17 excess ($\Delta^{17}$O) of nitrate, which is also termed mass-independent fractionation (MIF), cannot be changed or removed by subsequent mass-dependent fractionation processes and is thus conserved during atmospheric transport and processing (Brenninkmeijer et al., 2003; Vicars et al., 2013). So there will be no changes of $\Delta^{17}$O from HNO$_3$ to NO$_3^-$ As you comment, nitrate sometimes includes both inorganic nitrate and organic nitrate in the literature. However, only inorganic nitrate is analyzed in this study. This is due to that we separated...
dissolved inorganic nitrate from other anions (e.g., sulfate) by ion chromatography prior to analysis (He et al., 2018). According to the work of (Alexander et al., 2009), “Nitrate anion separation ensures that only inorganic nitrate is measured, assuming that soluble organic nitrate does not dissociate in water. Observations of C1-C5 alkyl nitrates in wet deposition (rain, snow, frost) (Hauff et al., 1998) suggest that they do not readily dissociate.” As for whether or not organic nitrate can be used by the denitrifying bacteria (Pseudomonas aureofaciens), the work of (Hawari et al., 2000) showed that biological degradation of RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) produced N₂O as a byproduct, suggesting that certain types of microorganisms can convert soluble organic nitrates into N₂O. However, it is not known whether or not Pseudomonas aureofaciens will do the same (Alexander et al., 2009).

2. Correlation between Δ¹⁷O(NO₃⁻) and [NO₃⁻]. It is plausible that the positive correlation is caused by that nocturnal pathways contribute more the [NO₃⁻]. However, how to explain that the correlation is degraded when [NO₃⁻] is > 50 μg m⁻³? Does it suggest that when [NO₃⁻] is high, NO₃⁻ is not from nocturnal pathways?

A: Thanks for your comments. We think the value of Δ¹⁷O(NO₃⁻) rather than the correlation between Δ¹⁷O(NO₃⁻) and [NO₃⁻] reflects the relative importance of nocturnal pathways. Take samples with [NO₃⁻] > 50 μg m⁻³ for example, their concentration-weighted Δ¹⁷O(NO₃⁻) is 31.3 ‰, which corresponds to nocturnal pathways’ possible fractional contribution of 56 – 100 % according to Eq. (4). This directly suggests NO₃⁻ is mainly from nocturnal pathways when [NO₃⁻] is high. In fact, the correlation between Δ¹⁷O(NO₃⁻) and [NO₃⁻] mainly reflects the relationship between their variations. NOR is high (0.40±0.06) when [NO₃⁻] is > 50 μg m⁻³, which suggests the rapid transformation of nitrate. Since visibility was always low with narrow variations (2.3±1.0 km), RH was always high with narrow range (67±7 %) and PM₂.₅ was always high (201±39 μg m⁻³) when [NO₃⁻] is > 50 μg m⁻³, the relative importance of nocturnal pathways can be rather stable along the rapid transformation of nitrate, which may account for the degraded correlation.

3. Section 3.4.4 is confusing. If coal combustion is the major contributor to NOx and coal combustion has the largest δ¹⁵N(NO₃⁻), why is the δ¹⁵N(NO₃⁻) very low (i.e., mostly ~0) in October?

A: Thanks for your comment. The work of (Zhang et al., 2007) and (Wang et al., 2012) suggest that
coal combustion and vehicles are the most two important contributor to NO\textsubscript{X} annually in north China. However the relative importance of different contributors varies with time. In winter heating seasons, which lasts from mid-November to mid-March, more coal is combusted for residential heating in north China. So the relative importance of coal combustion is higher in winter heating season than that in October. Since NO\textsubscript{X} emitted from vehicles can have $\delta^{15}\text{N(NO}_2\text{)}$ smaller than 0 ‰ (Walters et al., 2015), the higher contribution from vehicles in October than in winter heating season may account for the low $\delta^{15}\text{N(NO}_3\text{)}$ observed in October.

4. Many calculations are not clearly described. For example, line 214-217, it is not clear how these fractional values are calculated. Line 277, how is $[\delta^{15}\text{N(NO}_2\text{)}- \delta^{15}\text{N(NO}_X\text{)}]$ calculated? On a related note, what is the rationale to correlate $\delta^{15}\text{N(NO}_3\text{)}$ with $[\delta^{15}\text{N(NO}_2\text{)}- \delta^{15}\text{N(NO}_X\text{)}]$?

A: Thanks for your comments. In the work of (Alexander et al., 2009), the fractional values are calculated by the concentration of nitrate formed through different reaction pathways divided by the total concentration of inorganic nitrate, which are all modeled by GEOS-Chem model. In the work of (Michalski et al., 2003), the fractional values are the relative proportions of HNO\textsubscript{3} production by each reaction channel, which are modeled by a zero dimensional, time dependent, photochemical box model. $[\delta^{15}\text{N(NO}_2\text{)}- \delta^{15}\text{N(NO}_X\text{)}]$ equals to the right-hand side of Eq. (6), that's $(K-1)\times(1-f_{\text{NO}_2})$, where $K$ is obtained from the work of (Walters et al., 2016) and $f_{\text{NO}_2}$ is calculated by the mole concentration of NO\textsubscript{2} divided by the mole concentration of NO\textsubscript{X}. Please refer to the work of (Freyer et al., 1993) for more details of the derivation process of Eq. (6). Eq. (6) suggests that $[\delta^{15}\text{N(NO}_2\text{)}- \delta^{15}\text{N(NO}_X\text{)}]$ describes the isotopic exchange between NO and NO\textsubscript{2}. Since the isotopic exchange between NO and NO\textsubscript{2} can change $\delta^{15}\text{N}$ of NO\textsubscript{2}, the precursor of NO\textsubscript{3}, the positive correlation between $\delta^{15}\text{N(NO}_3\text{)}$ with $[\delta^{15}\text{N(NO}_2\text{)}- \delta^{15}\text{N(NO}_X\text{)}]$ is expected to suggest that the isotopic exchange between NO and NO\textsubscript{2} is likely to be an important factor for the variations of observed $\delta^{15}\text{N(NO}_3\text{)}$.

Minor Comments

1. Line 118-126. Show the estimated diurnal trends in the SI.

A: Thanks for your comment. The estimated diurnal trends are shown in Figure S1 now.

2. Section 2.4. Discuss the purpose of using MCM estimation.
A: Thanks for your comment. The purpose of using MCM estimation is to see whether the importance of nocturnal chemistry suggested by $\Delta^{17}O(NO_3^-)$ can be reproduced by models and to try to find potential reasons. We have added “To see whether the relative importance of nocturnal pathways constrained by $\Delta^{17}O(NO_3^-)$ can be reproduced by models,” in line 134 before “we use the standard Master Chemical Mechanism (MCM, version 3.3, http://mcm.leeds.ac.uk/) to simulate the mixing ratios of surface N$_2$O$_5$ and NO$_3$ radical during our sampling period.” in section 2.4

3. Line 194-203. The authors used two methods to estimate the alpha value. These two methods should be compared and the discrepancies should be discussed.
A: Thanks for your suggestions. We use observed $\Delta^{17}O(NO_3^-)$ to estimate the possible range of alpha, and use chemical kinetics to calculate specific alpha value to further estimate the relative importance of nocturnal pathways. As you know, in order to calculate specific alpha value, we estimated the concentrations of HO$_2$ and RO$_2$ radical. Our calculated specific alpha value based on the estimated concentrations of HO$_2$ and RO$_2$ radical is in the possible range of alpha constrained by observed $\Delta^{17}O(NO_3^-)$, which supports our further estimate of the relative importance of nocturnal pathways being reliable.

4. There are many gramma errors in the manuscript. For example, line 249, add “that” after “suggest”.
Sentences from line 304 to 306 and from line 263-267 have many gramma errors. These two sentences are too long and should be broken down. The authors should check throughout the manuscript.
A: Thanks for your suggestions. Grammar errors throughout the manuscript have been checked and corrected. Again, we have removed section 3.4 from the manuscript, which includes sentences from line 263-267. Sentences from line 304 to 306 have been changed into “Calculations with the constraint of $\Delta^{17}O(NO_3^-)$ suggest that nocturnal pathways (N$_2$O$_5 + H_2O/Cl$ – and NO$_3 + HC$) dominated nitrate production during polluted days (PM$_{2.5} \geq 75 \mu g m^{-3}$), with the mean possible contribution of 56 – 97 %.” in line 238-239.

Reference


Referee: J. Rudolph (Referee #2):

Comments: The paper presents an interesting example for the use of isotope ratio measurements to gain insight into complex atmospheric reaction systems, here the formation of nitric acid and nitrate from NOx. Overall the paper is well written, the experimental work and interpretation solid and the subject (particle formation by oxidation of primary atmospheric pollutants is relevant for air quality. I also appreciate that the authors openly explain that isotope ratio studies in complex systems can only provide constraints (here given as range of possible contributions to nitrate formation) and that additional information is required to fully understand the magnitude of contributions from different individual reaction pathways. Consequently, I recommend publication although the authors need to address some questions and uncertainties in more detail before the paper should be accepted for publication.

A: Thanks very much for your comments. We reply to your comments one by one as follows. One point needs to be addressed here is that we have removed section 3.4 from the manuscript due to that we are unable to explain the variations of $\delta^{15}N(NO_3)$ well so far.

Comments: 1. May main concern is that the paper does not consider the photolysis of NO$_2$ during daytime. Although this reaction is included in Figure 1 (R3), it is not considered in the excess oxygen calculation. During daytime the reaction sequence NO$_2$+$hv$=>$NO+O$ O+O$_2$=>$O_3$ NO+O$_2$=>$NO_2+O_2$ (R1) will result in a steady state which can (depending on photon flux and ozone concentration) be established within several minutes. This will result not only in an isotope exchange for N between NO
and NO₂ (Chapter 3.4.3) but also for O between NOₓ, O₂ and O₃. In contrast to this at night R1 is a one-way street. I do not know to which extent the daytime “recycling” of NO from NO₂ photolysis will impact the excess oxygen ratio in NO₂ and NO (and consequently in nitrate) or the ¹⁵N isotope ratio. Nevertheless, this is something that needs to be explained and discussed and potentially may change the interpretation of the isotope ratio measurements.

A: Thanks for your comment. The work of (Michalski et al., 2014) shows that, in both the light and dark simulations of NOₓ–O₂–O₃ system, the Δ¹⁷O values between NO₂ and NO were essentially equal within ±0.1‰. In this case, the final Δ¹⁷O value of NO₂ depends on the relative importance of O₃ oxidation in NO₂ production rates rather than photolysis. However, since simulation conditions have difference with the ambient conditions, future work should study whether or not photolysis alone can induce large diurnal difference in Δ¹⁷O(NO₂) at ambient conditions. As for the ¹⁵N isotope ratio, previous studies suggest N isotope exchange equilibrium between NO and NO₂ play an important role in δ¹⁵N of NO, NO₂ and atmospheric nitrate (Savarino et al., 2013; Freyer et al., 1993). Equation (6) suggest the partitioning of ¹⁵N between NO and NO₂ depends on the relative concentration of NO₂:NOₓ and the temperature-dependent isotope exchange constant. During the daytime, when NO and NO₂ coexist in NOₓ cycling, the N isotope exchange between NO and NO₂ can influence their individual δ¹⁵N (Freyer et al., 1993). At night, however, as NO is oxidized into NO₂ without photolysis, NO concentrations can be near zero when O₃ concentrations are high. In this case, NO₂ can reflects δ¹⁵N of local NOₓ sources, that’s NO₂:NOₓ approaches 1 and [δ¹⁵N(NO₂) – δ¹⁵N(NOₓ)] approaches 0 in Eq. (6). According to the work of (Walters et al., 2016), the lifetime of Leighton cycle reactions and NOₓ exchange can be comparable, therefore, the isotopic exchange between NO and NO₂ will be a mixture of these processes. The isotopic exchange associated with the NO + O₃ reaction and NO₂ photolysis has yet to be determined, so it will be a subject of future study. Due to that we are unable to explain the variations of δ¹⁵N(NO₃⁻) well, we have removed section 3.4 from the manuscript.

Comments: 2. The authors use several approximations and comparisons with published results (e.g. for estimating NO, the contribution of specific pathways of nitrate formation etc.). The validity of applying these published results for this study will depend on pollution levels, degree of impact of local sources, contribution from processed polluted air masses and so on and therefore may nor be directly applicable to the cases studied here. This needs to be explained and discussed in more detail.
A: Thanks for your suggestions. We are very sorry that some key species are not observed during our sampling period. When we use approximations to get their values, we try our best to let the approximations be reasonable or applicable for our cases. The estimate of α based on calculated HO₂ and RO₂ concentrations belongs to the first kind. Our estimated α, based on calculated HO₂ and RO₂ concentrations, is in the range of possible α values that directly derived from observed Δ¹⁷O(NO₃⁻) (Fig. 5) and is similar to the values determined in other mid-latitude areas (Michalski et al., 2003; Patris et al., 2007). So our estimated α on the base of calculated HO₂ and RO₂ should be reasonable. Besides, the subsequent estimate of fractional contribution of different nitrate formation pathways, which is based on estimated α and observed Δ¹⁷O(NO₃⁻), is a range but not a specific value. This range should be representative for the real situation. We have removed section 3.4, interpretation of δ¹⁵N(NO₃⁻) variations, from the manuscript.

Comments: 3. The various values (e.g. rate constants, excess isotope ratios in Table 2, estimates of [NO] from [CO]) used in the calculations will have uncertainties, which will add uncertainty to all quantitative results. This needs to be evaluated in more detail.
A: Thanks for your comment. It’s true that various values used in the calculations have uncertainties, and therefore add uncertainty to all quantitative results. However, as stated in the last answer, the estimated fractional contribution of different nitrate formation pathways is a range but not a specific value.

Comments: 4. Subchapter 3.4.1: Indeed, the impact of deposition on ¹⁵N is difficult to estimate. The argument that the impact of partitioning between gas and PM is minor since both HNO₃ and nitrate are collected on the filter is not convincing. Deposition rates for HNO₃ and nitrate differ and will be highly variable depending on the situation. If the ¹⁵N isotope ratios for PM nitrate and gas phase HNO₃ differ, differences in deposition rates will change the isotope ratio for the sum of HNO₃ and nitrate.
A: Thanks for your comment. Indeed, the impact of deposition on ¹⁵N is difficult to estimate during long range transport. In the present study, however, our sampling site is in megacity Beijing, which is the source region for NOₓ and atmospheric nitrate. So the impact of deposition on our observed δ¹⁵N(NO₃⁻) should be minor, especially when considering that no rains were observed except for a very small snow. We agree with your comment that deposition rates for HNO₃ and nitrate differ. However, when
considering the relatively short time of both HNO₃ and nitrate from being produced to being collected in our sampling site, we doubt that differences in deposition rates will not change the isotope ratio for the sum of HNO₃ and nitrate as much as that observed in remote areas (Geng et al., 2014). Again, we have removed section 3.4 from the manuscript.

Comments: 5. Chapter 3.4.3: This chapter neglects the NO+O₃ and NO₂+hv cycle (see above). Furthermore f_NOX (in Eq. 6) is based on [NO] values calculated from measured [CO] and [NO₂] and consequently the calculated values for [δ¹⁵N(NO₂) − δ¹⁵N(NO₃)] are in reality a non-linear function of the [NO₂] and [CO] concentrations. Thus Figure 7a is a plot of δ¹⁵N(NO₃⁻) versus a non-linear function of [NO₂] and [CO]. Not sure how to interpret this, but obviously [NO₂] and [CO] will vary for different sources with different ¹⁵N values. In order to be of value for the reader there needs a more detailed discussion than “should therefore be interpreted with the consideration of atmospheric contexts”. The discussion of δ¹⁵N(NO₃⁻) should be combined into one chapter discussing the different factors that may influence δ¹⁵N(NO₃⁻). Due to the complexity of the various factors influencing δ¹⁵N(NO₃⁻) the attempt to discuss individual contributions separately does not work well. A revised version considering these specific problems will merit publication.

A: Thanks very much for your comments. The influence of Leighton cycle on ¹⁵N can be summarized into the isotopic exchange constant K in Eq. (6) (Freyer et al., 1993). However, since the K value used in our study is determined from NO/NO₂ mixture without considering the influence of Leighton cycle (Walters et al., 2016), we truly neglects the NO+O₃ and NO₂+hv cycle. According to the work of (Walters et al., 2016), the lifetime of Leighton cycle reactions and NOX exchange can be comparable, therefore, the isotopic exchange between NO and NO₂ will be a mixture of these processes. The isotopic exchange associated with the NO + O₃ reaction and NO₂ photolysis has yet to be determined, so it will be a subject of future study. Due to that we are unable to explain the variations of δ¹⁵N(NO₃⁻) well, we have removed section 3.4 from the manuscript.

Details

General: Often a values are given as (xyz±abc), it is not always clear whether the ± indicates the error of the mean or the standard deviation.

A: Thanks for your reminding. The ± indicates the standard deviation and it has been illustrated in the
Correlations: If I understand correctly, the authors present r and not r². R values of 0.5 or so correspond to r² of 0.25, a very weak correlation. These low r values need a more critical discussion of their meaning. It maybe that even a weak correlation has statistical validity. However, it has to be remembered that for r=0.5, r²=0.25, which means that only 25% of the observed variability can be explained by a linear dependence between dependent and independent variable.

A: Thanks for your comments. These low r values is not discussed for their meaning in the present manuscript.

The authors use “wine colored” in several figure captions. Dark red would be better.

A: Thanks for your suggestion. The “wine colored” has been changed into “dark red” throughout the manuscript.

53: . And once formed
A: Thanks for your suggestion. We have corrected this error in line 53.

76: Sampling site
A: Thanks for your suggestion. We have corrected this error in line 74.

78: Super site set by..
A: Thanks for your suggestion. We have corrected this mistake in line 76.

81: About 10 km to our sampling site
A: Thanks for your suggestion. We have corrected this mistake in line 79.

88, 94: Insoluble substances were filtered (removed by filtration?)
A: Removed by filter membrane.

90: When determine the…
A: Thanks for your suggestion. We have corrected this mistake in line 88.

90: precision by our
A: Thanks for your suggestion. We have corrected this mistake in line 88.

95: which were decomposed from
A: Thanks for your suggestion. We have corrected this mistake in line 93.

110, 111 and other lines: is respectively
A: Thanks for your suggestion. We have corrected this mistake.

130: at the same time
A: Thanks for your suggestion. We have corrected this error in line 127.

133, 134: I assume weighted averages are meant. I understand the meaning and rational for concentration weighted oxygen excess, but I am not sure what production rate weighted means. $\alpha$ is a ratio with the total NO$_2$ production rate in the denominator, consequently the production rate weighted average for $\alpha$ would be some kind of average for the nominator, that is $k[NO][O_3]$. This requires more clarification and explanation.
A: Thanks for your comment. The production rate weighted $\alpha$ is calculated by

$$ \frac{\sum k_{R1}[NO][O_3]}{\sum (k_{R1}[NO][O_3] + (k_{R2a}[NO][NO_2] + (k_{R2b}[NO][RO_2]))} $$

for PD of each haze event.

164: samples
A: Thanks for your suggestion. We have corrected this error in line 160.

251: a small snow lasted for..
A: Thanks for your comment. We have removed this part for the manuscript.

258: ..it has been proposed that atmospheric nitrate that resulting from heterogeneous uptake of N…
A: Thanks for your comment. We have removed this part for the manuscript.

262: Don’t present similar trends.
A: Thanks for your comment. We have removed this part for the manuscript.

518: is set by
A: Thanks for your suggestion. We have corrected this error in line 444.

551: . And
A: Thanks for your suggestion. We have corrected this error in line 471.

Reference


G. Michalski (Referee #3):

Comments: A very interesting and exciting dataset. I think the manuscript would do well with some significant revisions.

A: Thanks very much for your comments. We reply to your comments one by one in the following part.

One point needs to be addressed here is that we have removed section 3.4 from the manuscript due to that we are unable to explain the variations of $\delta^{15}$N(NO$_3$) well so far.

Comments: Line 114 it is unclear to what the coefficients 24.85 and 13.66 mean or where they are derived. As someone versed in the field, and some information on line 26, I can surmise this is the $\Delta^{17}$O value NO$_2$+OH pathway, but this is in no way clear to the non-specialist. There are host of assumptions that go into this number that are not explained and have uncertainties that are not being propagated through. Six points on this are

1. From the text there is the assumption that the $\Delta^{17}$O of O$_3$ is essentially a fixed value of 26‰, which is by no means codified in the literature, despite the some who would hope so because it makes the data analysis less problematic.

2. Johnston et al. and Krankowsky et al. observed O$_3$ $\Delta^{17}$O values that spanned 18.8‰ to 41‰ with a standard deviation of 4.8‰.

3. Two papers by the Savarino group using a different method arrive at values close to 26‰ with smaller variations of 1 and 1.6‰. Their Antarctic paper noted O$_3$ $\Delta^{17}$O had “insignificant variation” 28 ‰ - 23 ‰, if one considers ~20% variation insignificant.

4. Lab experiments have clearly noted an O$_3$ $\Delta^{17}$O temperature dependence.

5. NO$_x$ photochemical equilibrium experiments (Michalski et al., 2013) a higher terminal atoms value transfer and Vicars noted that $\Delta^{17}$O(O$_3$)trans. in the range of 38–44‰ fits data.

6. Even assuming a fixed value of O$_3$ $\Delta^{17}$O value of 26‰, one cannot increase significant (24.85) digits by division/multiplication.

The authors should note these conflicting assumptions and how these assumptions would influence their interpretations of reaction pathways.
Thanks for your comment. The value of 24.85α and 24.85α + 13.66 in line 114 is respectively the Δ17O value NO2+OH and NO3+HC pathway (Table 1). To be clear for readers, we have added “By using the Δ17O assumptions for different pathways in Table 1 and the definition \( f_{R6} \times f_{R7} \times f_{R8} \times f_{R9} \times f_{R10} = 1 \), Eq. (1) is further expressed as” in line 110 before Eq. (2). And to be consistent with the significant digit of our assumption (Δ17O(O3) = 26 ‰), “24.85” and “13.66” have been changed into “25” and “14” respectively throughout the manuscript. We have learned that observed Δ17O values spanned largely in the work of (Krankowsky et al., 1995) and (Johnston and Thiemens, 1997) during the preparation of our manuscript. However, (Vicars and Savarino, 2014) questioned in their paper that “In the study of Krankowsky et al. (1995), no correlation was found between the δ17O and δ18O values of ozone, suggesting that the large degree of variability observed for Δ17O is an artifact resulting from statistical scatter of the individual d measurements. These results are therefore not inconsistent with the hypothesis that the tropospheric value of Δ17O(O3) is constant. However, the data of Johnston and Thiemens (1997) reveal a systematic variation in the relationship between δ17O and δ18O, with data from three different sites aligning on different slopes in a three-isotope plot. The authors of this study concluded that the observed variations resulted from differences in ozone transformation pathways between the three sites and suggested that measurements of the triple-isotope composition of ozone could therefore be useful in constraining the tropospheric ozone budget. This conclusion was later questioned by Brenninkmeijer et al. (2003), who argued that the differences in slope were not statistically significant and suggested that they were related to analytical bias.” In addition, Δ17O(O3) ≈ 26 ‰ from the observations of (Vicars and Savarino, 2014) and (Ishino et al., 2017) compare quite well in terms of average value: 25 ± 11 ‰ and 26 ± 5 ‰ for the studies of Krankowsky et al. (1995) and Johnston and Thiemens (1997) respectively, and the observations of (Vicars and Savarino, 2014) and (Ishino et al., 2017) are more recent publications, so we prefer Δ17O(O3) values reported by (Vicars and Savarino, 2014) and (Ishino et al., 2017). The assumption that Δ17O(O3) ≈ 26 ‰ is also adopted by (Chen et al., 2016). It’s true that lab experiments have clearly noted an O3 Δ17O temperature dependence. However, as (Vicars and Savarino, 2014) summed in their paper, “the experimentally determined dependency of Δ17O(O3) on the pressure of ozone formation suggests a relatively small decrease of only ~2 ‰ for an increase in pressure from 500 to 760 Torr (0.7 to 1.0 atm) (Morton et al.,1990; Thiemens and Jackson, 1990); and temperature dependency studies suggest an increase in Δ17O of only ~5 ‰ for an increase in ozone formation temperature from
260 to 320 K (Morton et al., 1990; Janssen et al., 2003). For these reasons, it is often assumed that $\Delta^{17}O(O_3)_{bulk}$ in the troposphere exhibits no more than a 1–2 ‰ level of variability under standard surface conditions”. Nevertheless, we noted that both (Vicars and Savarino, 2014) and (Ishino et al., 2017) uses the nitrite-coated filter technique in their studies, future studies may need other technique to verify whether $\Delta^{17}O(O_3)$ is truly constant in the surface atmosphere.

**Comments:** NO was derived CO mixing ratios derived from observations in winter Beijing (Lin et al., 2011). The correlation coefficients for this relationship are .76 and .82, which means there is some uncertainty in the derived NO. How would this impact the author’s results

A: Thanks for your comment. We realized that we are unable to explain $\delta^{15}N(NO_3)$ data well so far, and thus removed section 3.4 from the manuscript.

**Comments:** Line 200: “To estimate the specific $\alpha$ value, chemical kinetics in Table 2 and Eq. (3) were used. Specific $\alpha$ is estimated to range from 0.86 to 0.97 with a mean of (0.94±0.03)”. The coefficients used to estimate HO$_2$ has significant uncertainties (again r2= ~0.7) and the regression itself is are not universal but are valid for Tokyo. No discussion on whether this would hold in an extreme haze event in Beijing. Likewise the uncertainty of RO$_2$ = 0.7HO$_2$ must be significant and site specific. The validity of this assumption in the context of extreme haze needs to be discussed.

A: Thanks for your comment. As we all know, there are some similarities between Tokyo and Beijing, e.g., both of them are in the East and both of them are megacities, which increases the possible applicability of using the regression. In the regression, the HO$_2$ concentration is related with O$_3$ concentration (Kanaya et al., 2007), and we expect HO$_2$ concentration should be related with O$_3$ concentration too in Beijing as both HO$_2$ and O$_3$ are photochemical products whether or not in haze. Meanwhile, in the same season, the HO$_2$ concentration observed in Beijing (Liu et al., 2012) is generally comparable with that reported by (Kanaya et al., 2007) in Tokyo. If we double the estimated HO$_2$ and RO$_2$ concentrations, the calculated $\alpha$ would be 0.89±0.05. If we halve the estimated HO$_2$ and RO$_2$, the calculated $\alpha$ would be 0.97±0.02. Both of these two situation will not change the importance of nocturnal chemistry reported in the manuscript. As for RO$_2$ = 0.7HO$_2$, it’s the general value reported in the literature (Liu et al., 2012; Elshorbany et al., 2012; Mihelic et al., 2003). Neither double nor halve the value will change the importance of nocturnal chemistry reported in the
manuscript \( (\alpha = 0.92 \pm 0.04 \) and \( 0.95 \pm 0.02 \) respectively). In addition, Our estimated \( \alpha \), based on calculated \( \text{HO}_2 \) and \( \text{RO}_2 \) concentrations, is in the range of possible \( \alpha \) values that directly derived from observed \( \Delta^{17}\text{O(NO}_3^-) \) (Fig. 5) and is similar to the values determined in other mid-latitude areas (Michalski et al., 2003; Patris et al., 2007). So our estimated \( \alpha \) on the base of calculated \( \text{HO}_2 \) and \( \text{RO}_2 \) should be reasonable.

Comments: “lifetime of atmospheric nitrate is typically on the order of days (Vicars et al., 2013)” I doubt that Vicars was the first to determine the lifetime of nitrate in the atmosphere. Further the lifetime is significantly dependent on precipitation frequency so if there was no rain during the collection period the lifetime of nitrate is significantly longer, though it does not change the authors point.

A: Thanks for your reminding. We have changed the reference into an earlier one, i.e., (Liang et al., 1998).

Comments: 138 “We use the Master Chemical Mechanism “This requires an entire discussion section. MCM is a gas phase mechanism. Were heterogeneous reactions included? Based on what uptake scheme? How aerosol surface area was determined if that was part of the scheme? “1-h averaged mixing ratios of observed surface CO, NO\(_2\), SO\(_2\) and O\(_3\) and estimated NO” what does this mean? Did you initialize the model with these mixing ratios? Or did you correct the model to match these hourly? Or did you run the model hourly? What length of spin-up do you use? How was photolysis adjusted to account for haze? This model predicts things like OH\(_2\), RO\(_2\), NO…how does the model prediction compare with your estimation of these key compounds that we parameterized by your isotope scheme, but not measured? How does it predict things that were measured over time (O\(_3\), NO\(_2\))? This section was entirely too vague for anything useful to be inferred about the accuracy of predicted NO3 or N2O5 mixing ratios.

A: Thanks very much for your comments. The MCM model (version 3.3) we used is the standard one from the website (http://mcm.leeds.ac.uk/). The model includes heterogeneous reactions. However, we have no aerosol surface data as input. The 1-h averaged mixing ratios of observed surface CO, NO\(_2\), SO\(_2\) and O\(_3\) and estimated NO is used to initialize the model and these mixing ratios are updated every 12 hours. The model is set to output one dataset per hour. We did not adjust the photolysis to account
for haze, so the model predicted \( \text{HO}_{2} \) and \( \text{RO}_{2} \) is expected to be higher than the real value. In fact, the average of model predicted \( \text{HO}_{2} \) during the sampling period (including day and night) is 1.35 ppt, higher than our estimated value (0.88 ppt) by ~50%. Therefore we used the estimated value rather than the model predicted \( \text{HO}_{2} \) in our calculation due to that the estimated value is based on observed \( \text{O}_3 \) concentration. There also exist gaps between the measured \( \text{O}_3, \text{NO}_2 \) and predicted \( \text{O}_3, \text{NO}_2 \) (17 and 31 ppb vs 26 and 23 ppb respectively). This may due to that photolysis was not adjusted and the emission of \( \text{NO}_x \) was not considered during modeling. Since we use the standard MCM model only to get nocturnal radicals (\( \text{N}_2\text{O}_5 \) and \( \text{NO}_3 \)), the unadjusted photolysis may be not a major factor influencing predicted \( \text{NO}_3 \) or \( \text{N}_2\text{O}_5 \) mixing ratios. In addition, the variation trend of predicted \( \text{NO}_3 \) and \( \text{N}_2\text{O}_5 \) is a more useful information than the specific concentration in our study, which possibly deduce the risk of using this model in the present study.

Comments: “variation of atmospheric \( \delta^{15}\text{N}(\text{NO}_3) \) can be interpreted by the following four processes (Vicars et al.,2013)” again please give credit where credit is due, Freyer used this scheme 20 years before Vicars to investigate 15N variations in atmospheric nitrate.

A: Thanks for your reminding. This reference has been replaced by (Freyer, 1991).

Comments: 254 “The quartz filter used here is thought to collect both particulate nitrate and gaseous \( \text{HNO}_3 \)” this statement needs better justification by citing filter pack studies. This is particularly true in Beijing where \( \text{NH}_4\text{NO}_3 \) is a major component of PM and loss by volatilization could also be occurring. Vicars, like myself (2003), limited this assumption to coastal sampling where seas salt buffering was present and noted that “the exact nature of the nitrate species collected during sampling using glass fiber filters has always been an area of some debate due primarily \( \text{NH}_4\text{NO}_3 \).

A: Thanks very much for your reminding. We realized that the exact nature of the nitrate species collected during sampling using fiber filters has always been an area of some debate due primarily \( \text{NH}_4\text{NO}_3 \) and thus removed the statement from the manuscript.

Comments: Isotopic fractionations associated with nitrate formation pathways. These (Photolysis and KIE effects in NOy) are largely unknown and the discussion should reflect that. Walters ab initio paper indicates IF equilibrium is dominant the more oxidized compounds should have higher \( ^{15}\text{N} \). Is this
consistent with observations?

A: Thanks for your comment. It’s true that isotopic fractionations associated with nitrate formation pathways are largely unknown, so we decided to remove the entire section 3.4 from the manuscript. As for our observation, $\delta^{15}\text{N}(\text{NO}_3^-)$ is generally high (7.4±6.8 ‰), however, we do not know whether it is related to nitrate formation pathways. The $\delta^{15}\text{N}(\text{NO}_3^-)$ data is open for you if you are interested in haze in China.

Comments: 275 “Where K is the isotopic exchange constant of N between NO and NO$_2$, which is temperature-dependent ..” It is not clear if the authors are using temperature to calculate this daily, if so what temperature? Average? Day and night average? Clearly this equation is very dependent on fraction of NO$_2$, which is based on NO estimations that also have uncertainty, which should be discussed and represented on the y-axis error bar on figure 7. That caption should emphasize the Y data is not a measurement of the $\delta^{15}\text{N}$ of ambient NO$_2$ (Freyer, Walters) but a calculation. It would also seem that since the authors are presenting $\delta^{15}\text{N}$ in ‰, that the RHS of Eq. 6 will need to be multiplied by a factor of 1000.

A: Thanks for your comment. We uses the 12h-averaged temperature to calculate this. We cannot know how much the uncertainty of NO estimation influences the relationship between $\delta^{15}\text{N}(\text{NO}_3^-)$ and $[\delta^{15}\text{N}(\text{NO}_2) – \delta^{15}\text{N}(\text{NO}_X)]$, so we removed the entire section 3.4 from the present manuscript.

Comments: 279 “the correlation is better in residential heating season … especially in residential heating season. ” mechanistic, why would this so? The authors seem to imply residential heating is promoting exchange when its likely NO/NO2 ratios. Was the a correlation between $\delta^{15}\text{N}$ and $f_{\text{NO2}}$? The exchange section should discuss in terms of Freyers and Walters et al. papers that measured $\delta^{15}\text{N}$ values of ambient NO$_2$.

A: Thanks for your comment. I have no idea why the correlation is better in residential heating season, perhaps due to that source emission in residential heating season is more stable, leading to other factors, e.g., isotopic exchange, being more important for the trend of $\delta^{15}\text{N}(\text{NO}_3^-)$. Again, we removed the entire section 3.4 from the present manuscript.

Comments: “Influence of NO$_X$ emissions.” This section could be greatly expanded, there has been a
lot of recent work by the Elliot, Hastings, and Michalski groups of $^{15}$N sources. While coal maybe be dominant in the surrounding regions, automobiles and diesel trucks in Beijing must be significant, particularly during stagnant conditions. Is there a better N inventory for Beijing itself?

A: Thanks very much for your suggestions. It’s true that coal combustion and vehicles are the most important emissions in Beijing and its surrounding regions. We are sorry that we have not found better N inventory for Beijing, perhaps Qiang Zhang in Tsinghua University have the last inventory for Beijing.

Comments: I did not see any discussion about any (or lack thereof) correlation between $\delta^{18}$O $\Delta^{17}$O and $\delta^{15}$N. If they are completely decoupled then that would argue for source effects, if there is some covariation, then exchange/chemistry could be the main process.

A: Thanks for your comments. There is no correlation between $\Delta^{17}$O and $\delta^{15}$N (Fig. 4f), so we did not further discuss their relationship. The $\delta^{18}$O is highly positively correlated with $\Delta^{17}$O ($R^2 = 0.9$, data not shown), which means it may have almost the same implications with $\Delta^{17}$O, and thus we did not present the data of $\delta^{18}$O but $\Delta^{17}$O in the manuscript.

Reference


Johnston, J. C., and Thiemens, M. H.: The isotopic composition of tropospheric ozone in three


