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 ($N_2O_5 + H_2O$ 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_4NO_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

1

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 N_2O as a byproduct, suggesting that certain types of microorganisms can convert soluble organic nitrates into N_2O. However, it is not known whether or not Pseudomonas aureofaciens will do the same (Alexander et al., 2009).

2. Correlation between $\Delta^{17}O(NO_3^-)$ and $[NO_3^-]$. It is plausible that the positive correlation is caused by that nocturnal pathways contribute more the $[NO_3^-]$. However, how to explain that the correlation is degraded when $[NO_3^-]$ is > 50 μg m^{-3}? Does it suggest that when $[NO_3^-]$ is high, NO_3^- is not from nocturnal pathways?

A: Thanks for your comments. We think the value of $\Delta^{17}O(NO_3^-)$ rather than the correlation between $\Delta^{17}O(NO_3^-)$ and $[NO_3^-]$ reflects the relative importance of nocturnal pathways. Take samples with $[NO_3^-] > 50$ μg m^{-3} for example, their concentration-weighted $\Delta^{17}O(NO_3^-)$ is 31.3 ‰, which corresponds to nocturnal pathways' possible fractional contribution of 56 – 100 % according to Eq. (4). This directly suggests NO_3^- is mainly from nocturnal pathways when $[NO_3^-]$ is high. In fact, the correlation between $\Delta^{17}O(NO_3^-)$ and $[NO_3^-]$ mainly reflects the relationship between their variations. NOR is high (0.40±0.06) when $[NO_3^-]$ 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 $PM_{2.5}$ was always high (201±39 μg m^{-3}) when $[NO_3^-]$ 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 $\delta^{15}N(NO_3^-)$, why is the $\delta^{15}N(NO_3^-)$ 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_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_X emitted from vehicles can have $\delta^{15}N(NO_X)$ smaller than 0 ‰ (Walters et al., 2015), the higher contribution from vehicles in October than in winter heating season may account for the low $\delta^{15}N(NO_3^-)$ 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 $[\delta^{15}N(NO_2)- \delta^{15}N(NO_X)]$ calculated? On a related note, what is the rationale to correlate $\delta^{15}N(NO_3^-)$ with $[\delta^{15}N(NO_2)- \delta^{15}N(NO_X)]$?

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_3 production by each reaction channel, which are modeled by a zero dimensional, time dependent, photochemical box model. $[\delta^{15}N(NO_2)- \delta^{15}N(NO_X)]$ equals to the right-hand side of Eq. (6), that's $(K-1)\times(1-f_{NO2})$, where K is obtained from the work of (Walters et al., 2016) and f_{NO2} is calculated by the mole concentration of NO_2 divided by the mole concentration of NO_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 $[\delta^{15}N(NO_2)- \delta^{15}N(NO_X)]$ describes the isotopic exchange between NO and NO_2. Since the isotopic exchange between NO and NO_2 can change $\delta^{15}N$ of NO_2, the precursor of NO_3^-, the positive correlation between $\delta^{15}N(NO_3^-)$ with $[\delta^{15}N(NO_2)- \delta^{15}N(NO_X)]$ is expected to suggest that the isotopic exchange between NO and NO_2 is likely to be an important factor for the variations of observed $\delta^{15}N(NO_3^-)$.

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_2O_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 ($N_2O_5 + H_2O/Cl^-$ 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

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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 $NO_2+h\nu=>NO+O$ $O+O_2=>O_3$ $NO+O_3=>NO_2+O_2$ (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 NO$_2$ (Chapter 3.4.3) but also for O between NO$_X$, O$_2$ and O$_3$. 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 NO$_2$ photolysis will impact the excess oxygen ratio in NO$_2$ and NO (and consequently in nitrate) or the ^{15}N 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 NO$_X$–O$_2$–O$_3$ system, the Δ^{17}O values between NO$_2$ and NO were essentially equal within ±0.1‰. In this case, the final Δ^{17}O value of NO$_2$ depends on the relative importance of O$_3$ oxidation in NO$_2$ 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 Δ^{17}O(NO$_2$) at ambient conditions. As for the ^{15}N isotope ratio, previous studies suggest N isotope exchange equilibrium between NO and NO$_2$ play an important role in δ^{15}N of NO, NO$_2$ and atmospheric nitrate (Savarino et al., 2013; Freyer et al., 1993). Equation (6) suggest the partitioning of ^{15}N between NO and NO$_2$ depends on the relative concentration of NO$_2$/NO$_X$ and the temperature-dependent isotope exchange constant. During the daytime, when NO and NO$_2$ coexist in NO$_X$ cycling, the N isotope exchange between NO and NO$_2$ can influence their individual δ^{15}N (Freyer et al., 1993). At night, however, as NO is oxidized into NO$_2$ without photolysis, NO concentrations can be near zero when O$_3$ concentrations are high. In this case, NO$_2$ can reflects δ^{15}N of local NO$_X$ sources, that's NO$_2$/NO$_X$ approaches 1 and [δ^{15}N(NO$_2$) – δ^{15}N(NO$_X$)] approaches 0 in Eq. (6). According to the work of (Walters et al., 2016), the lifetime of Leighton cycle reactions and NO$_X$ exchange can be comparable, therefore, the isotopic exchange between NO and NO$_2$ will be a mixture of these processes. The isotopic exchange associated with the NO + O$_3$ reaction and NO$_2$ 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 δ^{15}N(NO$_3^-$) 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 HO_2 and RO_2 concentrations belongs to the first kind. Our estimated α, based on calculated HO_2 and RO_2 concentrations, is in the range of possible α values that directly derived from observed $\Delta^{17}O(NO_3^-)$ (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 α on the base of calculated HO_2 and RO_2 should be reasonable. Besides, the subsequent estimate of fractional contribution of different nitrate formation pathways, which is based on estimated α and observed $\Delta^{17}O(NO_3^-)$, 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 $\delta^{15}N(NO_3^-)$ 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 ^{15}N is difficult to estimate. The argument that the impact of partitioning between gas and PM is minor since both HNO_3 and nitrate are collected on the filter is not convincing. Deposition rates for HNO_3 and nitrate differ and will be highly variable depending on the situation. If the ^{15}N isotope ratios for PM nitrate and gas phase HNO_3 differ, differences in deposition rates will change the isotope ratio for the sum of HNO_3 and nitrate.

A: Thanks for your comment. Indeed, the impact of deposition on ^{15}N 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 NO_X and atmospheric nitrate. So the impact of deposition on our observed $\delta^{15}N(NO_3^-)$ 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 HNO_3 and nitrate differ. However, when

considering the relatively short time of both HNO$_3$ 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 HNO$_3$ 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+O$_3$ and NO$_2$+hv cycle (see above). Furthermore f_{NOx} (in Eq. 6) is based on [NO] values calculated from measured [CO] and [NO$_2$] and consequently the calculated values for [δ^{15}N(NO$_2$) – δ^{15}N(NO$_X$)] are in reality a non-linear function of the [NO$_2$] and [CO] concentrations. Thus Figure 7a is a plot of δ^{15}N(NO$_3^-$) versus a non-linear function of [NO$_2$] and [CO]. Not sure how to interpret this, but obviously [NO$_2$] and [CO] will vary for different sources with different ^{15}N 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 δ^{15}N(NO$_3^-$) should be combined into one chapter discussing the different factors that may influence δ^{15}N(NO$_3^-$). Due to the complexity of the various factors influencing δ^{15}N(NO$_3^-$) 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 ^{15}N 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/NO$_2$ mixture without considering the influence of Leighton cycle

(Walters et al., 2016), we truly neglects the NO+O$_3$ and NO$_2$+hv cycle. According to the work of

(Walters et al., 2016), the lifetime of Leighton cycle reactions and NO$_X$ exchange can be comparable,

therefore, the isotopic exchange between NO and NO$_2$ will be a mixture of these processes. The

isotopic exchange associated with the NO + O$_3$ reaction and NO$_2$ 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 δ^{15}N(NO$_3^-$)

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

manuscript in line 17 and 141.

Correlations: If I understand correctly, the authors present r and not r^2. R values of 0.5 or so correspond to r^2 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, r^2=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. α is a ratio with the total NO_2 production rate in the denominator, consequently the production rate weighted average for α 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 α is calculated by

$$\frac{\sum k_{R1}[NO][O_3]}{\sum(k_{R1}[NO][O_3]+(k_{R2a}[NO][HO_2]+(k_{R2b}[NO][RO_2])} \text{ for PD of each haze event.}$$

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

Freyer, H. D., Kley, D., Volz‑Thomas, A., and Kobel, K.: On the interaction of isotopic exchange processes with photochemical reactions in atmospheric oxides of nitrogen, J. Geophys. Res. Atmos., 98, 14791-14796, 1993.

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Savarino, J., Morin, S., Erbland, J., Grannec, F., Patey, M. D., Vicars, W., Alexander, B., and Achterberg, E. P.: Isotopic composition of atmospheric nitrate in a tropical marine boundary layer, Proc. Natl. Acad. Sci. USA, 110, 17668-17673, 2013.

Walters, W. W., Simonini, D. S., and Michalski, G.: Nitrogen isotope exchange between NO and NO2 and its implications for δ15N variations in tropospheric NOx and atmospheric nitrate, Geophys.

Res. Lett., 43, 440-448, 2016.

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.

A: Thanks for your comment. The value of 24.85α and 24.85α + 13.66 in line 114 is respectively the $\Delta^{17}O$ value NO_2+OH and $NO3+HC$ pathway (Table 1). To be clear for readers, we have added "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:" in line 110 before Eq. (2). And to be consistent with the significant digit of our assumption ($\Delta^{17}O(O_3) = 26$ ‰), "24.85" and "13.66" have been changed into "25" and "14" respectively throughout the manuscript. We have learned that observed $\Delta^{17}O$ 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 $\delta^{17}O$ and $\delta^{18}O$ values of ozone, suggesting that the large degree of variability observed for $\Delta^{17}O$ 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 $\Delta^{17}O(O_3)$ is constant. However, the data of Johnston and Thiemens (1997) reveal a systematic variation in the relationship between $\delta^{17}O$ and $\delta^{18}O$, 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, $\Delta^{17}O(O_3) \approx 26$ ‰ 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 $\Delta^{17}O(O_3)$ values reported by (Vicars and Savarino, 2014) and (Ishino et al., 2017). The assumption that $\Delta^{17}O(O_3) \approx 26$ ‰ is also adopted by (Chen et al., 2016). It's true that lab experiments have clearly noted an O_3 $\Delta^{17}O$ temperature dependence. However, as (Vicars and Savarino, 2014) summed in their paper, "the experimentally determined dependency of $\Delta^{17}O(O_3)$ 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 $\Delta^{17}O$ 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 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)". 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 α would be 0.89±0.05. If we halve the estimated HO_2 and RO_2, the calculated α 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; Mihelcic et al., 2003). Neither double nor halve the value will change the importance of nocturnal chemistry reported in the

manuscript (α = 0.92±0.04 and 0.95±0.02 respectively). In addition, Our estimated α, based on calculated HO_2 and RO_2 concentrations, is in the range of possible α values that directly derived from observed $\Delta^{17}O(NO_3^-)$ (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 α on the base of calculated HO_2 and 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 (O3, 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 HO_2 and RO_2 is expected to be higher than the real value. In fact, the average of model predicted 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 HO_2 in our calculation due to that the estimated value is based on observed O_3 concentration. There also exist gaps between the measured O_3, NO_2 and predicted O_3, 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 NO_X was not considered during modeling. Since we use the standard MCM model only to get nocturnal radicals (N_2O_5 and NO_3), the unadjusted photolysis may be not a major factor influencing predicted NO_3 or N_2O_5 mixing ratios. In addition, the variation trend of predicted NO_3 and N_2O_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 $\delta^{15}N(NO_3^-)$ 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 HNO3" this statement needs better justification by citing filter pack studies. This is particularly true in Beijing where NH4NO3 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 NH4NO3.

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 NH_4NO_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}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, $\delta^{15}N(NO_3^-)$ is generally high (7.4±6.8 ‰), however, we do not know whether it is related to nitrate formation pathways. The $\delta^{15}N(NO_3^-)$ 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 δ15N of ambient NO_X (Freyer, Walters) but a calculation. It would also seem that since the authors are presenting $\delta^{15}N$ 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 $\delta^{15}N(NO_3^-)$ and $[\delta^{15}N(NO_2) – \delta^{15}N(NO_X)]$, 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 $\delta^{15}N$ and f_{NO2}? The exchange section should discuss in terms of Freyers and Walters et al. papers that measured $\delta^{15}N$ 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 $\delta^{15}N(NO_3^-)$. 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.

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