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* *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.*

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