Thank you for your constructive comments that help improve the discussion. We carefully revised the initial manuscript according to reviewers' comments and point-by-point responses are given as follows. In the revised manuscript, changes are shaded in yellow. Responses are based on the revised manuscript.

Anonymous Referee #1

In elucidating the behavior of nitrate (NO_3^-) contained aerosol, research using stable isotope ratios has been actively conducted in recent years. In particular, the study of the $\delta^{15}N$ (NO_3^-) and $\Delta^{17}O$ (NO_3^-) of $PM_{2.5}$ in Seoul from 2018 to 2019 to quantitatively estimate the oxidation pathways of particulate NO_3^- and the source apportionment of major NOx emission sources is a very innovative and academically valuable study. However, even though discussing dual isotopes, they were not being discussed effectively. In addition, several issues were raised, such as the lack of clarity in the explanation of many of the discussions. Therefore, it could not be accepted by Atmospheric Chemistry and Physics international journal.

Major points
1. The studies on the environmental kinetics using $\Delta^{17}O$ (NO_3^-) and the source analysis using $\delta^{15}N$ (NO_3^-) were not organically linked. For example, how was the source contribution affected by the use of $\Delta^{17}O$ (NO_3^-) in the source analysis? How did the use of $\Delta^{17}O$ (NO_3^-) to elucidate the environmental dynamics affect the source contribution? It be made clearer how it was clarified and how the findings differed from past studies?

It has been of great interest to elucidate the chemical cycling of NO_y and its production and loss because of difficulties in measuring N_xO_y species and their labile nature between gaseous and particle phase. To make it complicated, NH_3 adds to the difficulty in understanding the formation pathway of particulate nitrate. In this respect, isotopes are really useful tools for tracing its emission sources and chemical transformation pathways of reactive nitrogen oxide gases to particulate nitrate. For nitrate, $\Delta^{17}O$ and $\delta^{15}N$ are good indicators that can quantitatively distinguish HNO_3 oxidation processes and NO_x emission sources, respectively, which is important to air quality policy. As you pointed out, however, these two individual methods have not yet fully integrated, especially due to the poor understanding of the gas-to-particle conversion process and limited information on the

isotope fractionation effect during oxidation reactions.

So far, several studies have applied $\delta^{15}N$ and $\delta^{18}O$ methods to understand the origin and transformation of atmospheric NO_3^-. Some of them took the method to estimate fractional contributions of major oxidation pathways responsible for HNO_3 formation by utilizing $\delta^{18}O$ (NO_3^-) and then quantitatively apportion NO_x sources based on $\delta^{15}N$ (NO_3^-) signatures and existing $\delta^{15}N$ values of NO_x source endmembers by applying the fractional contributions of oxidation pathways (Chang et al., 2018; Song et al., 2019; Zong et al., 2017). However, during NO_y photochemical cycling and its loss processes, $\delta^{15}N$ and $\delta^{18}O$ of initial NO_x can be significantly altered by both kinetic and equilibrium isotopic fractionation effects (ε_N), complicating the link between nitrate $\delta^{15}N$ and $\delta^{18}O$ and the precursor NO_x (Michalski et al., 2004; Michalski et al., 2003). In specific, N_2O_5 pathway was solely considered as a nighttime pathway and ε_N was calibrated by applying a constant factor without a clear explanation of the $\delta^{15}N$ and $\delta^{18}O$ methods in several studies (Chang et al., 2018; Song et al., 2019; Zong et al., 2017). As a result, their ε_N was distinctively higher relative to ε_N retrieved from $\Delta^{17}O$, leading to different source contributions by more than a factor of 2 (Song et al., 2020).

In this study, we determined $\Delta^{17}O$ (NO_3^-) of NO_3^- in $PM_{2.5}$, a conserved tracer of atmospheric NO_3^- (Michalski et al., 2003; Savarino et al., 2008; Thiemens, 2006) and quantified proportional contributions of three major oxidation pathways (namely, OH pathway and O_3 pathways associated with N_2O_5 and NO_3 radical; renamed as "R4", "R7", and "R8" pathway, respectively in the revised manuscript) to the measured NO_3^- (Sect. 2.3.2): 87% OH oxidation pathway in summer and 38% O_3 oxidation pathway in winter (24% N_2O_5 and 14% NO_3 radical). The fractional contribution of O_3 oxidation pathway increased up to 70% on polluted days with daily $PM_{2.5}$ mass concentration exceeding 75 $\mu g\ m^{-3}$. This result is consistent with those from ambient measurements conducted in Seoul. Brown et al. (2017) made tower measurements on the mountain in Seoul using a cavity enhanced spectroscopy and found that nitrate radical production rate was much greater in Seoul than in Los Angeles. Jordan et al. (2020) reported that nitrate production was about a factor 3 higher during the haze period relative to the other period due to enhanced nighttime nitrate production involving heterogeneous N_2O_5 hydrolysis.

We finally calculated ε_N by applying the $\Delta^{17}O$-based proportions of three major NO_3^- oxidation pathways and considered it to estimate $\delta^{15}N$ of atmospheric (NO_2) from the measured $\delta^{15}N$ (NO_3^-) (Eqs. 4-1 and 4-2). Figure 5 illustrates the measured $\delta^{15}N$ (NO_3^-) and estimated $\delta^{15}N$ (NO_2), which are compared with $\delta^{15}N$ values of NO_x source

endmembers. Regardless of season, most $\delta^{15}N$ (NO_2) was close to the $\delta^{15}N$ domain of vehicle emission NO_x, indicative of vehicle emissions as a dominant emission source in urban Seoul. Consistently, the national NO_x bottom-up emissions inventory, the Clean Air Policy Support System (CAPSS), shows a total mobile source (>60 %) as the largest anthropogenic source in Seoul metropolitan area. Actually, some of the winter $\delta^{15}N$ (NO_3^-) values without consideration of isotope fractionation effect are indicative of coal emission sources, demonstrating that these results could otherwise mislead conclusions about major NO_x sources.

Combining our results with the previous findings, it is clear that the $\delta^{15}N$ and $\Delta^{17}O$ pair is a more robust approach for quantitatively assessing the NO_x source contribution to atmospheric NO_3^- compared to the method of a single $\delta^{15}N$ or $\delta^{15}N$ and $\delta^{18}O$ pair.

L73-77:

Despite evidences that $\delta^{15}N$ (NO_x) can serve as a useful tracer of NO_x emission sources, during NO_y photochemical cycling and its loss processes, the $\delta^{15}N$ of initial NO_x can be significantly altered by both kinetic and equilibrium isotopic fractionation effects (ε_N), complicating the link between $\delta^{15}N$ (NO_3^-) and $\delta^{15}N$ (NO_x) (Freyer et al., 1993; Li et al., 2020).

L104-106:
These N isotope fractionation effects should be first evaluated to explore NO_x source contributions, which should be based on combining with a robust tracer for the contributions of NO_3^- oxidation pathways.

2. The estimated source contribution should be discussed more quantitatively from the viewpoint other than isotope, because biomass burning is very large. Research on isotopes is still unexplored, and it is thought that it will be put to practical use only after such discussions.

You are right. It is our concern, too.

From satellite observation, Seoul Metropolitan Area has been identified as one of the NO_2 hop spots over the world. Although its concentration has lately been decreasing, the annual average concentration is still above 20 ppbv (Seoul Metropolitan Government). Moreover, there is discrepancy between bottom-up and top-down emission inventories

(e.g.,Goldberg et al., 2019). Regarding it, there have been debates going on. Possible candidates are biomass combustion for agricultural clearing and heating, and transported sources for long distances.

Air quality of Northeast Asia including urban atmospheres is frequently influenced by various types of biomass burning, such as agricultural fires in spring and fall, open forest fire in summer, and domestic heating in winter, throughout the year (Chen et al., 2017). Therefore, we considered biomass burning as one of the major NO_x emission sources potentially affecting air quality in Seoul, and in Figure 5, we illustrated the mean $\delta^{15}N$ value of NO_x produced by biomass burning of various biomass types in laboratory experiments (Fibiger and Hastings, 2016). To our knowledge, these $\delta^{15}N$ (NO_x) values are first existing dataset made from controlled combustion setting with various biomasses. However, as mentioned by the authors, the $\delta^{15}N$ (NO_x) varied among biomass types from -7 to 12‰ and thus major biomass type potentially affecting air quality in Seoul should be considered. In the present study, $\delta^{15}N$ measurements of biomass-burning-produced NO_x are not available in Seoul.

Furthermore, we have reviewed previous studies in urban China reporting NO_x source apportionment results using the Bayesian isotope mixing model based on $\delta^{15}N$ and $\delta^{18}O$ measurements of atmospheric NO_3^-. The contribution of biomass burning ($\delta^{15}N$- NO_x from Fibiger and Hastings, 2016) was estimated as 20-30%, while contributions of coal combustion and soil emissions were seasonally varying with high coal- and high soil-contributions in winter and in summer, respectively (Fan et al., 2020; Song et al., 2020; Zong et al., 2020). These results are suggestive of the inherent uncertainty of the isotope mixing model and/or the need of realistic source endmember $\delta^{15}N$ (NO_x) from biomass burning in application of the isotope mixing model.

In the revised manuscript, NO_x source apportionment using a Bayesian stable isotope mixing model is removed in Sect. 3.4. and instead, source contribution is discussed qualitatively. In the future study, source endmember $\delta^{15}N$ (NO_x) values should be investigated by direct measurements in Seoul and surrounding areas to test the validity of $\delta^{15}N$-based NO_x source apportionments, following the robust method to measure $\delta^{15}N$ and $\Delta^{17}O$ of NO_x (Albertin et al., 2021; Walters et al., 2018). Since 2021, GEMS (Geostationary Environment Monitoring Spectrometer; Kim et al., 2020) satellite started to play an active role in producing NO_2 observation data (https://nesc.nier.go.kr/), which will help to find the solution.

L503-511:

This study region is under influence of various biomass burning sources throughout a year, such as agricultural combustion in vicinities of Seoul and over eastern China from spring to fall (Chen et al., 2017; Zhao et al., 2017), wild fires over Siberia and Russian Far East in summer (van der Werf et al., 2010), and residential biomass combustion for heating over east Asia in winter. Some winter $\delta^{15}N$ $(NO_x)_{atmosphere}$ values fell in the $\delta^{15}N (NO_x)$ range of biomass burning endmember (Fibiger and Hastings, 2016; Figure 5). When assessing contributions of biomass burning based on $\delta^{15}N (NO_x)_{atmosphere}$ and few endmember $\delta^{15}N (NO_x)$, however, caution should be exerted considering the fact that $\delta^{15}N (NO_x)$ varied among biomass types from -7 to 12‰ (Fibiger and Hastings, 2016) and there is currently a lack of understanding of biomass combustion that could potentially affect air quality in Seoul.

L526-537 in Conclusions and outlook:

While our results demonstrate that $\delta^{15}N$ and $\Delta^{17}O$ are robust tracers for major NO_x sources, quantitative source apportionment using the isotope method requires further elaboration of isotope equilibrium/kinetic fractionation effects involved in photochemical cycling of nitrogen oxides and $\delta^{15}N$ of NO_x source endmembers representing local or regional emissions in East Asia. In well-designed field studies, the $\delta^{15}N$ and $\Delta^{17}O$ measurements of multiphase and their vertical structures allow us to test the isotope fractionation effects suggested by laboratory experiments and theoretical calculations, and to characterize the atmospheric processing that influence them. In addition, there is an urgent need to document the $\delta^{15}N (NO_x)$ values of emission sources from vehicles with/without selective catalytic reduction (SCR) and from biomass combustion as a function of biomass type and combustion conditions. Consequently, a comprehensive and quantitative understanding of the oxidation pathways and emission sources of nitrogen oxides using $\delta^{15}N$ and $\Delta^{17}O$ measurements will be able to elucidate detailed mechanisms driving severe haze development in megacities of northeast Asia, including Seoul.

3. Many of the figures were characteristic figures, and many of them were very difficult to understand.

Figures are redrawn for readability of audience.

In addition, the other points are shown below.

4. Introduction part: It would be better to discuss isotope-related research and other research separately. In addition, Line 40 is an introduction to isotope-related research, and these should be discussed separately.

Isotope-related research and other research are discussed separately.

5. Lines 89-97: Please move to the method part.

It is moved to line 69-73.

6. Lines 98-113: The introduction of the research on $\Delta_{17}O$ ($NO_{3−}$) should be described more clearly. Please rewrite.

It is rewritten.
L107-123:

Lately, $\Delta^{17}O$ (NO_3^-) has been used for tracing NO_3^- oxidation pathways (Alexander et al., 2009, 2020; Morin et al., 2009; Savarino et al., 2007, 2013). Earlier researches observed atmospheric NO_3^- is anomalously enriched in ^{17}O (Michalski et al., 2003), which stems from O_3 formation reactions, where a rare isotope effect leads to excess ^{17}O enrichment relative to what is expected based on the ^{18}O enrichments (Thiemens, 1999, 2006). This enrichment is quantified by $\Delta^{17}O$ notation (^{17}O-excess, defined as $\delta^{17}O−0.52×\delta^{18}O$). Since non-zero $\Delta^{17}O$ strictly reflects a photochemical effect, NO_3^- produced by denitrification in soils should have $\Delta^{17}O$ of zero. The mass-independent $\Delta^{17}O$ signature of O_3 is transferred to NO_x, in which the number of oxygen atom from O_3 is involved in NO_x. In this way, the $\Delta^{17}O$ (NO_3^-) is served as a conservative marker to track the chemical formation of atmospheric NO_3^-. Photochemical formation by peroxy radicals (HO_2 and RO_2) leads to a relatively low $\Delta^{17}O$ (NO_3^-), whereas nighttime formation through N_2O_5 and NO_3 results in high $\Delta^{17}O$ (Michalski et al., 2003; Morin et al., 2009; Savarino et al., 2007). Consequently, the difference in $\Delta^{17}O$ (NO_3^-) suggests approaching a proportional contribution of daytime and nighttime oxidation of NO_3^-.

To date, few field studies have coupled $\Delta^{17}O$ (NO_3^-) and $\delta^{15}N$ (NO_3^-) to investigate NO_x-to-NO_3^- oxidation processes and emission sources of NO_x, e.g., field researches in Japan (Nelson et al., 2018), west Virginia USA (Rose et al., 2019), Shanghai , China (He et al., 2020) and Beijing, China (He et al., 2018; Song et al., 2020).

7. Line 123: Table 1 should be added in line.

One of summer samples was not measured (due to over-scale) and thus the number of summer samples is re-written as 13 in Table 1.

8. Lines 147-157: For the analysis method of $\Delta_{17}O$ (NO_{3-}), it is stated to refer to Morin, 2009, but more details should be written.

We don't think it is necessary to develop in more detail the analytical method. The bacterial decomposition of nitrate and the further thermal decomposition of the N_2O produced by the bacteria is now recognized as a standard method and has been detailed and cited in many times nitrate isotope studies. To further guide the reader to updated method we add the McIlvin reference (McIlvin and Casciotti, 2011), which is an updated of the Casciotti original publication. However, we have complemented the description by adding the use of the thermal decomposition of N_2O which was not mentioned in the original manuscript (but effectively presents in Morin et al 2009). The text now reads as

L168-171:

==The analytical procedure used in this study strictly followed the method described in Morin et al. (2009) which adheres to the now standard bacterial method coupled with the gold catalyst for the thermal decomposition of N_2O into N_2 and O_2 (Kaiser et al., 2007).==

Line 156: Is the standard deviation the mean of the standard deviations, or does it mean within that number? Please describe clarify.

This is now clarified as followed:

The overall accuracy of the method is estimated as the reduced standard deviation of the residuals from the linear regression between the measured reference materials and their expected values (Morin et al. 2009). For these sets of analyses, the obtained uncertainties values (1σ) were 0.4 ‰ and 0.3 ‰ for $\Delta^{17}O(NO_3^-)$ and $\delta^{15}N(NO_3^-)$, respectively.

9. Lines 162-164: It is not clear whether it is two steps or three steps. Please make the

description clearer.

It is rewritten.

Lines 176-177:

The HNO_3 forms through three major pathways including (i) OH pathway, (ii) O_3 pathway associated with N_2O_5, and (iii) O_3 pathway associated with NO_3.

10. Line 267: Shouldn't source data be added here?

NO_x source apportionment using a Bayesian stable isotope mixing model is removed in Sect. 3.4. and source contribution is discussed qualitatively. Therefore, source data is presented in Sect. 1 introduction and Sect. 3.4.

11. Section 3.1: There were few comparisons with previous papers, and more consideration should be given to the reliability and characteristics of the data. In particular, the discussion of isotopes after line 306 should be revised, since it only compares figures and does not refer to references.

It is revised.

L318-340:

Both $\delta^{15}N$ (NO_3^-) and $\Delta^{17}O$ (NO_3^-) exhibited an inverse correlation with ambient temperature (r= -0.87 and r= -0.55, respectively). The $\delta^{15}N$ (NO_3^-) exhibited higher values in winter with a weight-mean of -0.7‰ ± 3.3 ‰ and 3.8‰ ± 3.7 ‰ in the summer and the winter, respectively. This seasonal pattern of $\delta^{15}N$ (NO_3^-) has been typically observed in East Asia regions (Li et al., 2019; Song et al., 2019; Zong et al., 2020). Analysis of backward airmass trajectory indicates that the lower and the upper bound of $\delta^{15}N$ (NO_3^-) were associated with air masses from the ocean by southerly and easterly winds in the summer and from Siberia by northerly winds in winter, respectively (Figure S3). In comparison with urban China (Figure 2a), averaged summer $\delta^{15}N$ (NO_3^-) values were comparable between Seoul and all urban Chinese sites reported here, whereas in winter, $\delta^{15}N$ (NO_3^-) of Seoul was similar to those of Shanghai and Guangzhou rather than $\delta^{15}N$ (NO_3^-) of Beijing that were higher than 10‰. Another observation at a mountain station in Taiwan shows that the highest $\delta^{15}N$ (NO_3^-) was found in spring when the level of

anthropogenic constituents were elevated (Guha et al., 2017). These observations over East Asia may suggest at some extent that the seasonal pattern of $\delta^{15}N$ (NO_3^-) is basically associated with synoptic meteorological condition that controls the type and strength of emission sources, where low and high $\delta^{15}N$ (NO_3^-) values indicate biogenic soil emissions and fossil-combustion, respectively. (Elliott et al., 2019)(Elliott et al., 2019)

Along with nitrogen isotope, heavier oxygen isotopes were also enriched in NO_3^- during the winter compared to the summer, when the weight-mean of $\delta^{17}O$, $\delta^{18}O$, and $\Delta^{17}O$ in NO_3^- were 70.4‰ ± 5.4 ‰, 82.0‰ ± 6.2 ‰, and 27.7‰ ± 2.2 ‰ for the winter and 57.3‰ ± 4.9 ‰, 65.7‰ ± 6.2 ‰, and 23.2‰ ± 2.2 ‰ for the summer. These results of high winter and low summer $\Delta^{17}O$ (NO_3^-) were consistent with previous observations at urban Beijing (He et al., 2018; Wang et al., 2019b; Figure 2b), indicative of relatively greater contribution of nighttime oxidation pathways in winter. It is also noteworthy that our summer and winter $\Delta^{17}O$ (NO_3^-) values were similar to annual $\Delta^{17}O$ (NO_3^-) values of an urban (Sapporo) and a rural (Rishiri) site in Japan, respectively (Nelson et al., 2018). It is likely suggestive that the winter $\Delta^{17}O$ value in Seoul has undergone a considerable atmospheric processing on a regional scale.

12. Line 320: high relative humidity? Please describe clearly and statistically.

L342-346:

Clearly, for the winter samples with $PM_{2.5}$ concentration greater than 40 μg m^{-3}, meteorological conditions varied relative to low $PM_{2.5}$ samples; relatively high temperature and RH staying at 0 ℃ to 10 ℃ and 45 % to 65 %, respectively, and low wind speed of 1 m s^{-1} to 2 m s^{-1}, representing the meteorological characteristics of winter $PM_{2.5}$ episodes.

13. Line 452-Line 461: This part should be included in the section3.1? Isn't it better to summarize the discussion of source analysis in this section?

The paragraph is moved into Sect. 3.1.

Please see the response to comment 11.

14. Line 476-479: Please move the method part.

NO_x source apportionment using a Bayesian stable isotope mixing model is removed in

Sect. 3.4. and source contribution is discussed qualitatively. Therefore, source data is presented in Sect. 1 introduction and Sect. 3.4.

15. Line 479-482: I would like you to clearly describe the discussion on the difference between the case where fractionation is considered and the case where it is not.

NO_x source apportionment using a Bayesian stable isotope mixing model is removed in Sect. 3.4.

16. Figure 2: The figure was very difficult to understand. Rather than this figure, a scatter diagram may provide clearer discussion.

The figure is modified as suggested and renumbered as figure 3.
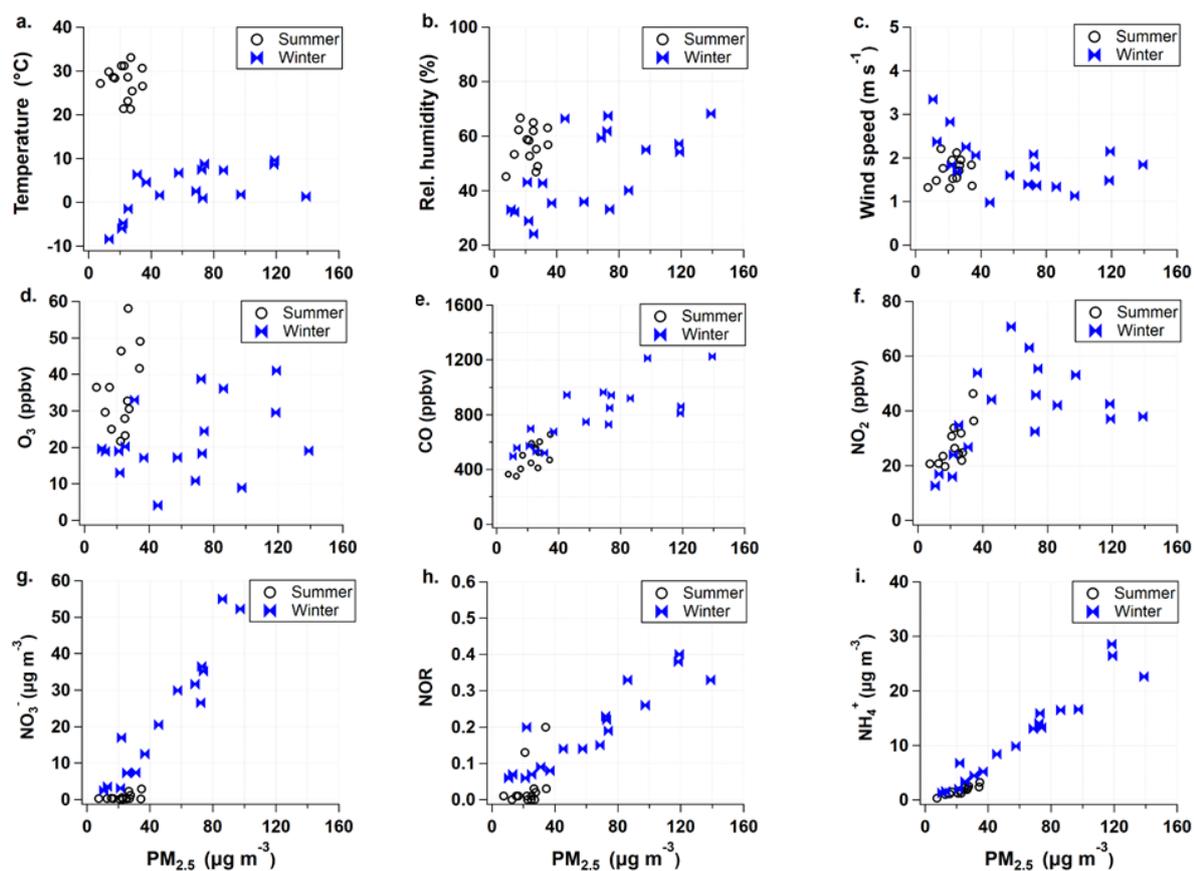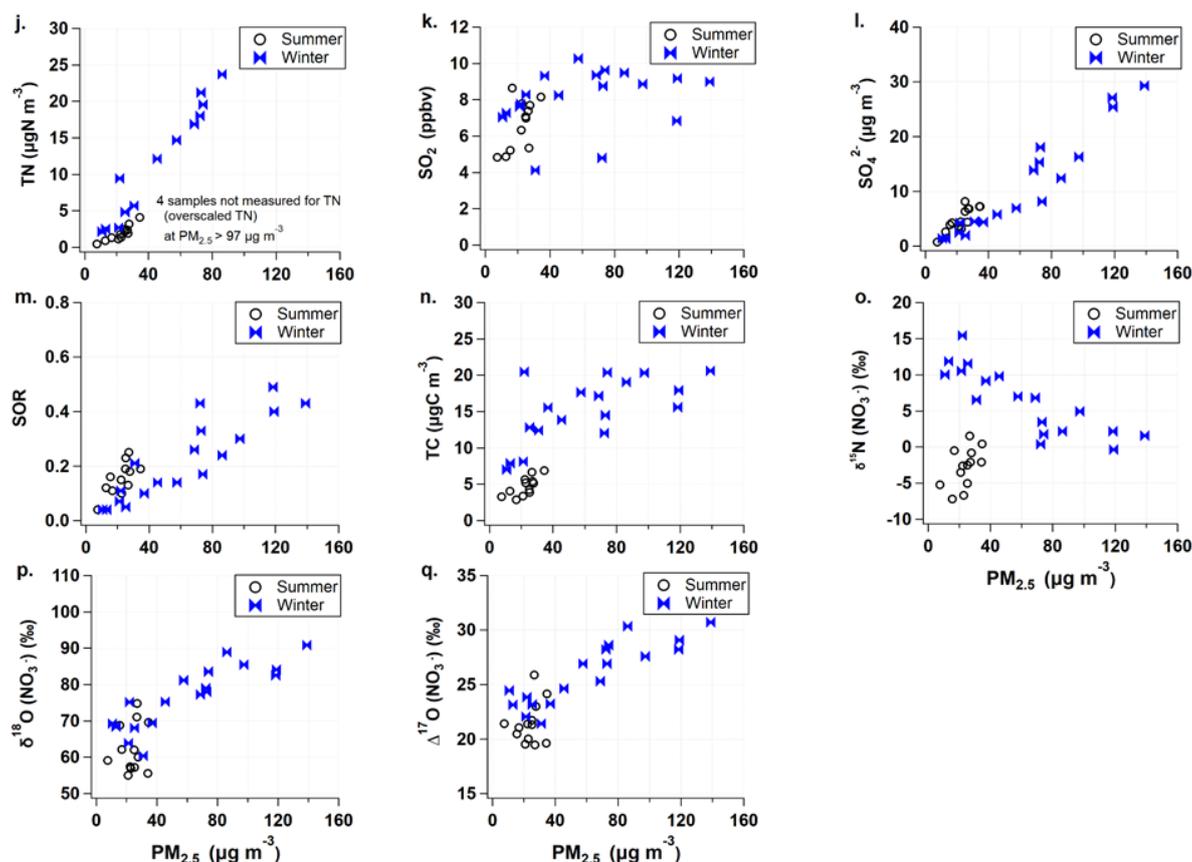
Figure 3. Relationships of PM$_{2.5}$ mass concentration with meteorological parameters (a-c), concentrations of reactive gases (d-f, k) and aerosol chemical constituents (g-j, l-n), and N and O isotopic compositions (o-q) measured in Seoul during the summer (open circle) and the winter (blue ribbon).

Related discussion is also rewritten as follows.
L332-342:

Given that PM$_{2.5}$ concentrations reflect the seasonality, atmospheric chemical composition and meteorological properties were examined in relation to PM$_{2.5}$ concentrations (Figure 3). Clearly, for the winter samples with PM$_{2.5}$ concentration greater than 40 μg m^{-3}, meteorological conditions varied relative to low PM$_{2.5}$ days; relatively high temperature and RH staying at 0℃ to 10℃ and 45% to 65%, respectively, and low wind speed of 1 m s^{-1} to 2 m s^{-1}, representing the meteorological characteristics of winter PM$_{2.5}$ episodes. Particularly in winter, a strong linearity of PM$_{2.5}$ was found with most

chemical constituents considered in this study, such as SIA species, TN, NOR, and SOR. However, although being elevated in levels, NO_2 and O_3 mixing ratios showed non-linearity with $PM_{2.5}$ concentrations. Isotope ratios were correlated either linearly or inversely with $PM_{2.5}$ concentrations. In winter, $\Delta^{17}O$ (NO_3^-) showed the best correlation with $PM_{2.5}$ concentrations but $\delta^{15}N$ (NO_3^-) was inversely related with $PM_{2.5}$ level.

17. Figure 3: The figure was very difficult to understand. The comparison of sources is made, but is it the data of Rose, 2019? Do you consider isotope fractionation?

In the submitted manuscript, dotted boxes in the figure are the ranges of potential endmember values of $\Delta^{17}O$ (NO_3^-) for R4, R7, and R8 pathways and corresponding $\delta^{15}N$ (NO_x) of NO_x sources, considering isotope fractionation. However, the figure including all these information is difficult to read, as pointed out by the reviewer. Thus, these figures were replaced with those presented below and discussed endmember values of $\Delta^{17}O$ (NO_3^-) and $\delta^{15}N$ (NO_x) separately. The former was illustrated in Figure 4a and b as black dotted boxes and the latter was shown in Figure 5.
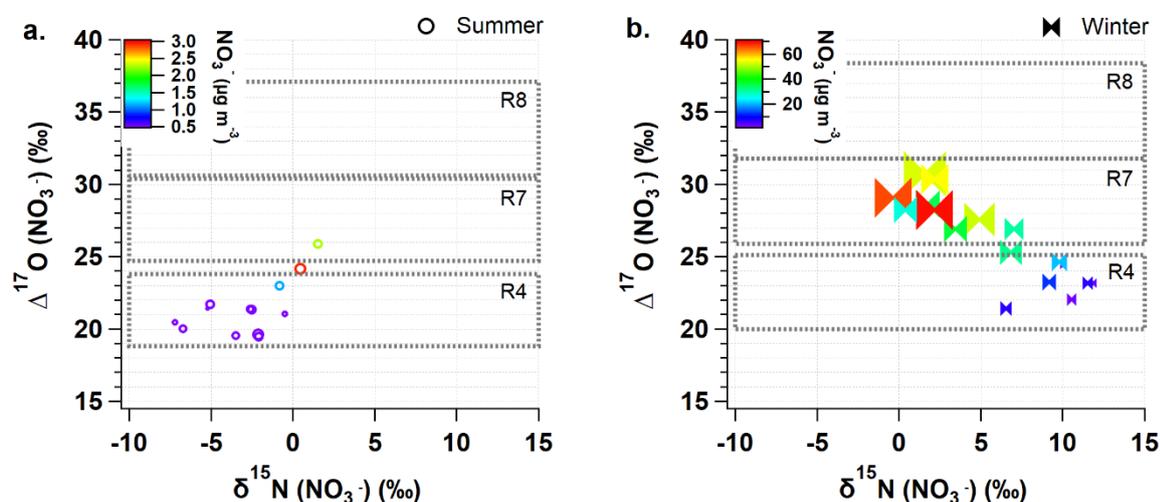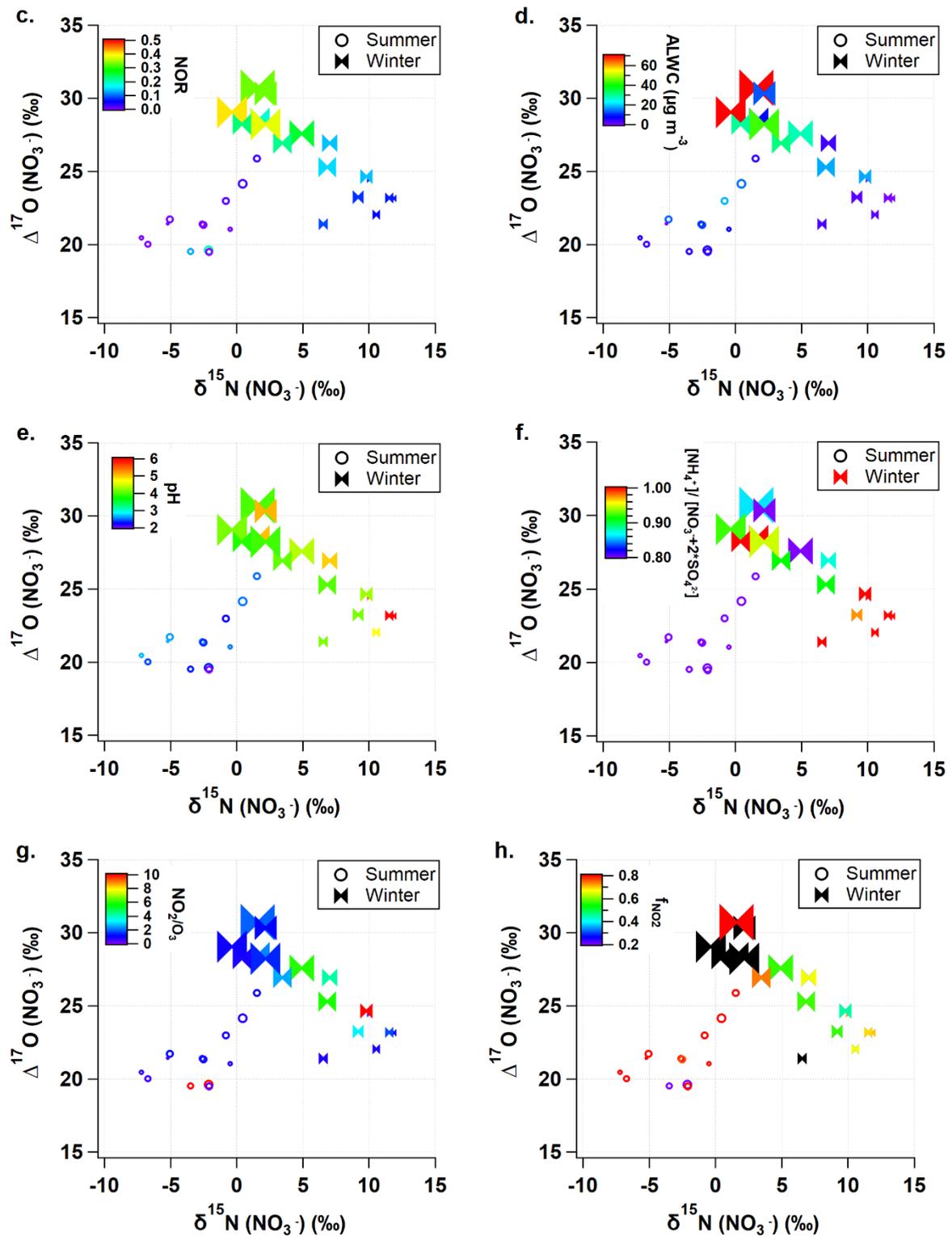
Figure 4. The relationship of measured $\delta^{15}N$ (NO_3^-) and $\Delta^{17}O$ (NO_3^-) values with key parameters during the summer (open circle) and winter (closed ribbon). The predicted $\Delta^{17}O$ (NO_3^-) values are presented as dotted rectangles for the tree major NO_3^- formation pathways

(R4, R7, and R8, see Sect. 2.3.2 for details) in (a) summer and (b) winter. Data are color coded by (a) and (b) nitrate concentrations, (c) NOR, (d) ALWC, (e) pH, (f) $[NH_4^+]/([SO_4^{2-}]+[NO_3^-])$ equivalent ratio, (g) NO_2/O_3 ratio, and (h) f_{NO2}. Marker size is proportional to PM$_{2.5}$ concentration ranging from 10 μg m^{-3} to 100 μg m^{-3}.
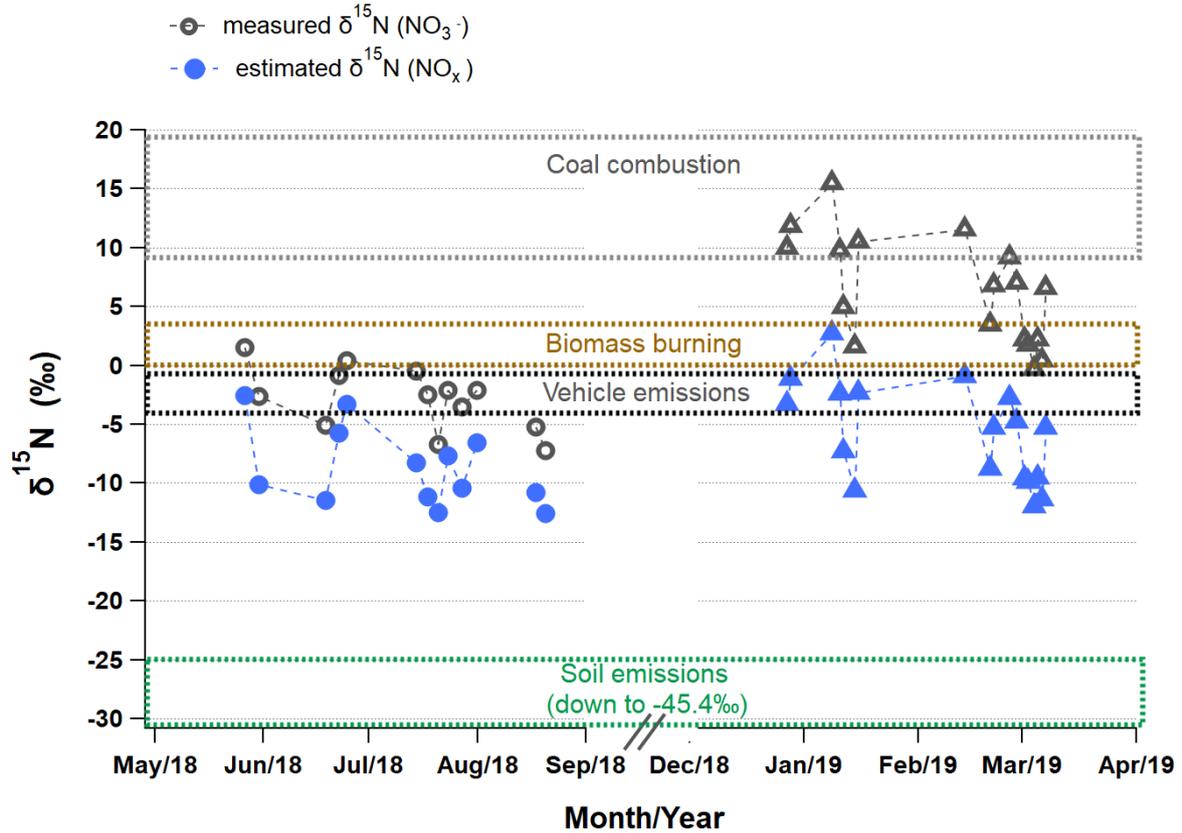
Figure 5. Variations in measured δ^{15}N (NO$_3^-$) (open) and estimated δ^{15}N (NO$_x$)$_{atmosphere}$ (closed) in Seoul during the summer (circle) and winter (triangle). The δ^{15}N (NO$_x$) range (mean ± 1sd) of source end members are distinguished by dotted boxes in different colors: coal combustion (14.2 ± 4.5 ‰) (Felix et al., 2012; Heaton, 1990), biomass burning (1.8 ±1.8 ‰) (Fibiger and Hastings, 2016), vehicle emissions (-2.5 ± 1.5 ‰) (Walters et al., 2015), and biogenic soil emissions (-35.1 ± 10.2 ‰) (Felix and Elliott, 2014; Li and Wang, 2008; Yu and Elliott, 2017).

Anonymous Referee #2

In this study by Lim et al., the authors measured the D17O and d15N of atmospheric nitrate particulates in Seoul, Korea during two different seasons and used this isotopic information to understand the oxidation formation pathways of atmospheric nitrate and to source partition NOx emission sources. The basic rationale is to estimate the relative fractions of the three major nitrate oxidation pathways using the conversative D17O tracer and then use these fractions, along with the relevant nitrogen isotope effects (mostly derived from theoretical calculations), to re-construct the original d15N of ambient NOx. This isotope effect-corrected d15N-NOx signal can then be combined with d15N-NOx source signatures to source partition local NOx emissions. While I found this research important and timely, and that the analysis and discussions related to the D17O of nitrate are thorough and convincing, there are multiple flaws and ambiguities in the discussion of the d15N data.

1. First, nitrogen isotope effects that are important for the conversion of gaseous NOx to particulate nitrate are not clearly discussed and treated during the data analyses and discussion. The first of those is the nitrogen isotope effect for the Leighton NOx cycle. The authors used a lumped isotope effect of 1.018 to represent the combined kinetic and equilibrium isotope effect for the photochemical NO-NO2 cycling. However, this value was determined by simultaneous d15N-NO2 and d15N-NOx in a very different atmospheric environment (in terms of NOx concentration, NO-to-NO2 ratio, and O3 concentration; i.e., Julich Germany) (Freyer et al., 1993). How this value is representative to the study site of this work is unknown. More importantly, this value is an annual average, without considering temperature effects. A following laboratory study confirming this value (Li et al., 2020) was also conducted at room temperature. Because seasonal temperature fluctuations likely have strong effects on nitrogen isotopic fractionations in the atmosphere (Walters and Michalski, 2015), these impacts need to be acknowledged and considered during the nitrogen isotope data correction. This is a particularly important issue for this study as the temperature effects are expected to manifest to different extent in the data collected during the summer and winter seasons.

You are absolutely right.

Both the N isotope effects occurring during NO$_x$ photochemical cycle and the N equilibrium

isotopic exchange between NO and NO_2 are important, determining $\delta^{15}N$ of NO_x in the atmosphere. However, both isotopic effects have not been well constrained.

The relative importance of either fractionation may vary depending on atmospheric conditions such as NO_2/NO_x ratio, NO_x/O_3 ratio, and ambient temperature (Freyer et al., 1993; Li et al., 2020). In urban atmospheres with high NO_x concentrations, N isotope equilibrium between NO and NO_2 has been suggested to play an important role in their N isotope partitioning by ambient measurements and laboratory experiments-based studies (Freyer et al., 1993; Li et al., 2020; Walters et al., 2016).

In the present study, a positive and a negative correlation of $\delta^{15}N$ (NO_3^-) with $[NO_2]/[O_3]$ moral ratio ($R^2=0.52$) and ambient temperature ($R^2=0.76$) likely indicate the significant role of N isotope equilibrium reaction between NO and NO_2, which is compatible to the previous findings.

Freyer et al. (1993) inferred a combined (day and night) N isotope fractionation factor between NO and NO_2 ($^{15}\alpha_{NO2/NO}$), 1.018 ± 0.001, based on 1-year measurements of NO_x concentrations and $\delta^{15}N$ (NO_2) at Julich. This factor is smaller than laboratory-measured $^{15}\alpha_{NO2/NO}$ associated with N isotopic equilibrium reaction, 1.0289 ± 0.0019 at room temperature (Li et al., 2020) or 1.0356 ± 0.0015 (Walters et al., 2016). Given that N isotope equilibrium is most likely the dominant reaction leading to N isotope fractionation between NO and NO_2 and temperature effect should be considered for it, we adopted temperature-dependent $^{15}\alpha_{NO2/NO}$ (Walters et al., 2016) to determine N isotope fractionation effect of pathway (i). This method resulted in $^{15}\alpha_{NO2/NO}$ of 1.036-1.038 for summer and of 1.041-1.046 for winter samples and accordingly, corresponding ε_1 of $5.9\pm1.5‰$ and of $12.2\pm0.5‰$. Finally, the net N isotope fractionation effect ($\varepsilon_N = \varepsilon_1 + \varepsilon_2 + \varepsilon_3$) is applied to estimate the $\delta^{15}N$ (NO_x) in the atmosphere.

L200-201:

$^{15}\alpha_{NO2/NO}$ is the ==temperature-dependent== isotope equilibrium exchange fractionation factor for NO_2/NO (Walters et al., 2016).

L459-466:

To investigate major emission sources of atmospheric NO_x in Seoul, $\delta^{15}N$ (NO_x) in the atmosphere ($\delta^{15}N$ ($NO_x)_{atmosphere}$) was estimated from measured $\delta^{15}N$ (NO_3^-) considering nitrogen isotopic fractionation effects (ε_N) based on a dual isotopes approach ($\Delta^{17}O$ and $\delta^{15}N$). Estimated ε_N values were 5.9 ± 1.5 ‰ and of 12.2 ± 0.5 ‰ and accordingly, the $\delta^{15}N$ ($NO_x)_{atmosphere}$ was -8.7 ± 3.3 ‰ and -5.8 ± 4.2 ‰ in summer and winter, respectively. The larger winter ε_N reveals the enhanced contribution of nighttime oxidation pathway via N_2O_5. As a result, a seasonal difference in $\delta^{15}N$ ($NO_x)_{atmosphere}$ was as small as 2.9 ‰ on average, which is suggestive of little seasonal difference in major NO_x emission source in Seoul.

2. It is also not clear how the isotope effect for the NO2-OH oxidation was represented during the data analysis. In several places, the authors claimed that this step exerts no isotope effect; in some other places, a small isotope effect of -3 permil was mentioned (e.g., Line 182-184). The empirical and/or theoretical grounds for these deductions were not sufficiently stated.

Since N isotope equilibrium between NO and NO_2 is likely the dominant reaction leading to N isotope fractionation, and kinetic isotope effect associated with the reaction between NO_x and OH is relatively too small (-3‰), we assumed no kinetic isotope effect associated with the reaction between NO_x and OH, as done in literatures (e.g., Chang et al., 2018; Rose et al., 2019; Song et al., 2019). In addition, please note that we assigned reaction numbers to the three major oxidation pathways, i.e., (OH pathway and O_3 pathways associated with N_2O_5 and NO_3 radical as "R4", "R7", and "R8" pathway, respectively) in the revised manuscript.

Line 195-197:
The N fractionation effect of particulate NO_3^- produced via HNO_3 (R4) pathway (ε_1, unit in ‰) can be expressed as the following, neglecting kinetic isotope effects associated with HNO_3 (R4) pathway (Walters and Michalski, 2016):

3. Furthermore, the isotope effect for the conversion from gaseous HNO3 to particulate nitrate was completed ignored. A previous study found that the isotope effect for this gasto-solid conversion step dominated the variability of atmospheric nitrate aerosols, was dependent on aerosol pH, and can be potentially as large as 22 permil (Geng et al., 2014). In general, I found more work is needed to better consider the large uncertainties surrounding the nitrogen isotope effects during the d15N data correction. While some of

these uncertainties have been mentioned in this manuscript, failures to incorporate these uncertainties into the NOx source partitioning invalidates the partitioned results. Consequently, these results should be deemed only qualitative, but not quantitative. In this sense, a thorough sensitivity analysis, like the one used to treat NOx source signatures, is required to tackle these uncertainties associated with the nitrogen isotope effects.

Few studies have conducted simultaneous $\delta^{15}N$ measurements of gaseous HNO_3 and particulate NO_3^- (E.g., Kawashima, 2019; Nelson et al., 2018; Savard et al., 2017). Their N isotope fractionation effect ($\varepsilon_{HNO3 \rightarrow p\text{-}NO3\text{-}}$) is about 5‰ on average. However, individual samples varied in $\varepsilon_{HNO3 \rightarrow p\text{-}NO3\text{-}}$, likely depending on atmospheric concentrations of NO_x, HNO_3, and other precursor gases, aerosol pH, ambient temperature, etc, which are poorly constrained yet. In order to minimize uncertainties in N isotope fractionation effect between NO_2 and NO_3^- and corresponding NO_2 source apportionment, we removed the results of quantitative source apportionment using the Bayesian isotope mixing model and discussed qualitatively about major NO_x sources in Sect. 3.4. in the revised manuscript. In addition, Geng et al. (2014) studied nitrate in Greenland snow, where $\delta^{15}N$ signature was dominated by long-range transport process to the Arctic, which is not compatible to the $\delta^{15}N$ signature found in the urban atmosphere.

Uncertainties involved in N isotope fractionation effect should be resolved in future field research in parallel to theoretical calculations and laboratory experiments, which is discussed in Conclusion section as follows.

L526-537:
Conclusions and outlook

While our results demonstrate that $\delta^{15}N$ and $\Delta^{17}O$ are robust tracers for major NOx sources, quantitative source apportionment using the isotope method requires further elaboration of isotope equilibrium/kinetic fractionation effects involved in photochemical cycling of nitrogen oxides and $\delta^{15}N$ of NO$_x$ source endmembers representing local or regional emissions in East Asia. In well-designed field studies, the $\delta^{15}N$ and $\Delta^{17}O$ measurements of multiphase and their vertical structures allow us to test the isotope fractionation effects suggested by laboratory experiments and theoretical calculations, and to characterize the atmospheric processing that influence them. In addition, there is an urgent need to document the $\delta^{15}N$ (NO$_x$) values of emission sources from vehicles with/without selective catalytic

reduction (SCR) and from biomass combustion as a function of biomass type and combustion conditions. Consequently, a comprehensive and quantitative understanding of the oxidation pathways and emission sources of nitrogen oxides using δ^{15}N and Δ^{17}O measurements will be able to elucidate detailed mechanisms driving severe haze development in megacities of northeast Asia, including Seoul.

Minor comments:

[1] 87-89: The mention of negative fractionation effect here is very confusing. First, you need to define what a positive (or normal) isotope effect is and then to assign either a positive or a negative sign to indicate positive/negative isotope effects.

For clarity, a negative fractionation effect is expressed as with "-" symbol, with respect to a positive effect.

L103-104:

On the other hand, the nitrogen partitioning between NO_2 and NO_3 (R5) may induces a fractionation effect of about -18‰ (Walters and Michalski, 2015).

[2] 172-179: Throughout the manuscript, it is not clear how this A factor was derived using in situ data and used to correct d15N data.

Li et al. (2020, 2021) proposed A factor, defined as $\tau_{exchange}/\tau_{NO2+h\nu} = j_{NO2}/ k_1 \times [NO]$ ($k_1 = 8.14 \times 10^{-14}$ cm^3 s^{-1}, Sharma et al., 1970), to evaluate the relative importance of equilibrium isotopic effect (EIE) and Leighton cycle isotope effect (LCIE) to δ^{15}N(NO$_2$). This factor does not directly correspond to N isotope fractionation factor, $^{15}\alpha_{NO2/NO}$.
It is clarified as follows.

L189-190:

In Seoul, to simply evaluate the relative importance of EIE and LCIE only (not for ^{15}N correction), A factor was estimated to be 0.08 ± 0.20 (median $\pm$ standard deviation) and 0.60 ± 0.51 during the winter and summer months, respectively, indicating the significant influence of the equilibrium isotope effect on NO-NO$_2$ isotopic fractionation. The time series j_{NO2} was calculated using the Master Chemical Mechanisms (MCM) (Saunders et al., 2003) model.

[3] 182-184: this sentence is difficult to follow. Did you assume no fractionation during NO2-OH oxidation or use -3 permil for this step? Need more clarifications.

It is clarified as follows.

Line 195-197:

The N fractionation effect of particulate NO_3^- produced via HNO_3 (1) pathway (ε_1, unit in ‰) can be expressed as the following, neglecting kinetic isotope effects associated with HNO_3 (R4) pathway (Walters and Michalski, 2016):

[4] 264: I understand these source endmembers were presented somewhere else in the paper. But to ease readability, I would suggest including several sentences or a table here to summarize or contrast the different d15N ranges.

NO_x source apportionment using a Bayesian stable isotope mixing model is removed in Sect. 3.4. and source contribution is discussed qualitatively in the revised manuscript. Therefore, corresponding source data is presented only in Sect. 1 introduction and Sect. 3.4.

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