Response to the referee #1 (egusphere-2023-744)

Dear Lei Geng,

We thank you for your valuable review of this work and relevant comments that greatly improved the manuscript. Your comments/suggestions are given below in bold, followed by our answers. Changes/new elements added to the manuscript are presented in blue.

Major comments:

1) **The way to derive RO_2 using measured $\Delta^{17}O(NO_2)$: I don't think it make any sense to use the other method (i.e., Case B) to estimate RO_2 and compare the results with Case A.**

First of all, as shown in Table 1, in both SP1 and SP2, neither the derived RO_2 concentra4onat each sampling period nor the averages can be considered as "consistent"; Don't get the points how can these values can be called "closeness".

Secondly, to derived RO_2 from $\Delta^{17}O(NO_2)$ (i.e., Case A), one simply assumes that it is only RO_2 completes with O_3 to oxidize NO as indicated by Equation 13. This ignores the contributions of HO_2. While in Case B, a RO_2/HO_2 ratio of 0.859 was applied. So does this mean that in Case A the same ratio of RO_2/HO_2 can also be applied and then compared with Case B? In fact, it is highly doubtable that the same ratio in one study can be applied to another, given variations in concentrations of CO, CH_4 and NMVOCs, don't even to mention the uncertainties associated with the empirical formula of HO_2 calculation using O_3.

So just saying from $\Delta^{17}O(NO_2)$ to estimate RO_2 and note it is actually representing the sum of RO_2 and HO_2 is enough here. This provides a new method to estimate RO_2 and HO_2 radicals, and can be verified with actual measurements in the future. The current way of Case B is just too uncertain and the results are not comparable.

Thank you for pointing this out, which was also a concern for Reviewer #2. We agree with your comments and have removed the comparison with Case B in the revised version of the manuscript which now only discusses RO_2 derived from isotopic measurements. We invite you to read our answers to Reviewer #2 pages 26-27 and pages 30-32, where you will find the revised manuscript structure and the reworded/modified section 3.2 on isotopically derived RO_2.

The authors paid too much attentions to the observations of Beijing and tried to make analogies between the two in order to explain their observations. However, the authors overlooked the differences in concentrations of $PM_{2.5}$, PM_{10} and nitrate between the two days, and all of these concentrations in SP 2 are higher in SP 2 than SP 1, would this suggest a transport events and non-local sources of nitrate? Note the $\delta^{15}N(NO_3^-)$ values and its relationship with $\delta^{15}N(NO_2)$ are also different in SP 2 compared to SP 1, this may indicate the same thing: a regional transport event occurred and which brought non-local nitrate. The $\delta^{15}N$ and $\Delta^{17}O$ data should be combined to discuss at this point.

We were not sought to draw analogies but rather to show how an interpretation of $\Delta^{17}O(NO_3^-)$ variabilities without taking into account of the stratification of $\Delta^{17}O(NO_2)$ at night in polluted environments could lead to biased conclusions. We believe it is important to alert the community on such over-interpretations, which could arise from poor considerations of $\Delta^{17}O(NO_2)$ dynamics.

The last, references or other evidence should be provided when attributed the high load of PM_{10} in SP 2 to Saharan dust, e.g., back trajectory analysis or something similar.

The Saharan dust episode which began around 23 February was indeed more diffuse that that of 7 February. NASA AQUA MODIS satellite images show the formation of a dusty air mass over the Saharan region on February 20 and the displacement of this air mass over the following days towards the south of France (**Erreur ! Source du renvoi introuvable.**). In addition, backtracking trajectory (HYSPLIT) shows the air mass from the south entering the Chamonix valley on 24 February (**Figure 1**). Figure 1 and 2 have been added to the revised Supplement.

To note, we had visual evidence of the presence of Saharan dust in the Chamonix atmosphere during SP 2 and the extractions from the GF filters collected during SP 2 showed a yellow coloration, very distinct from the filter extractions from SP 1.
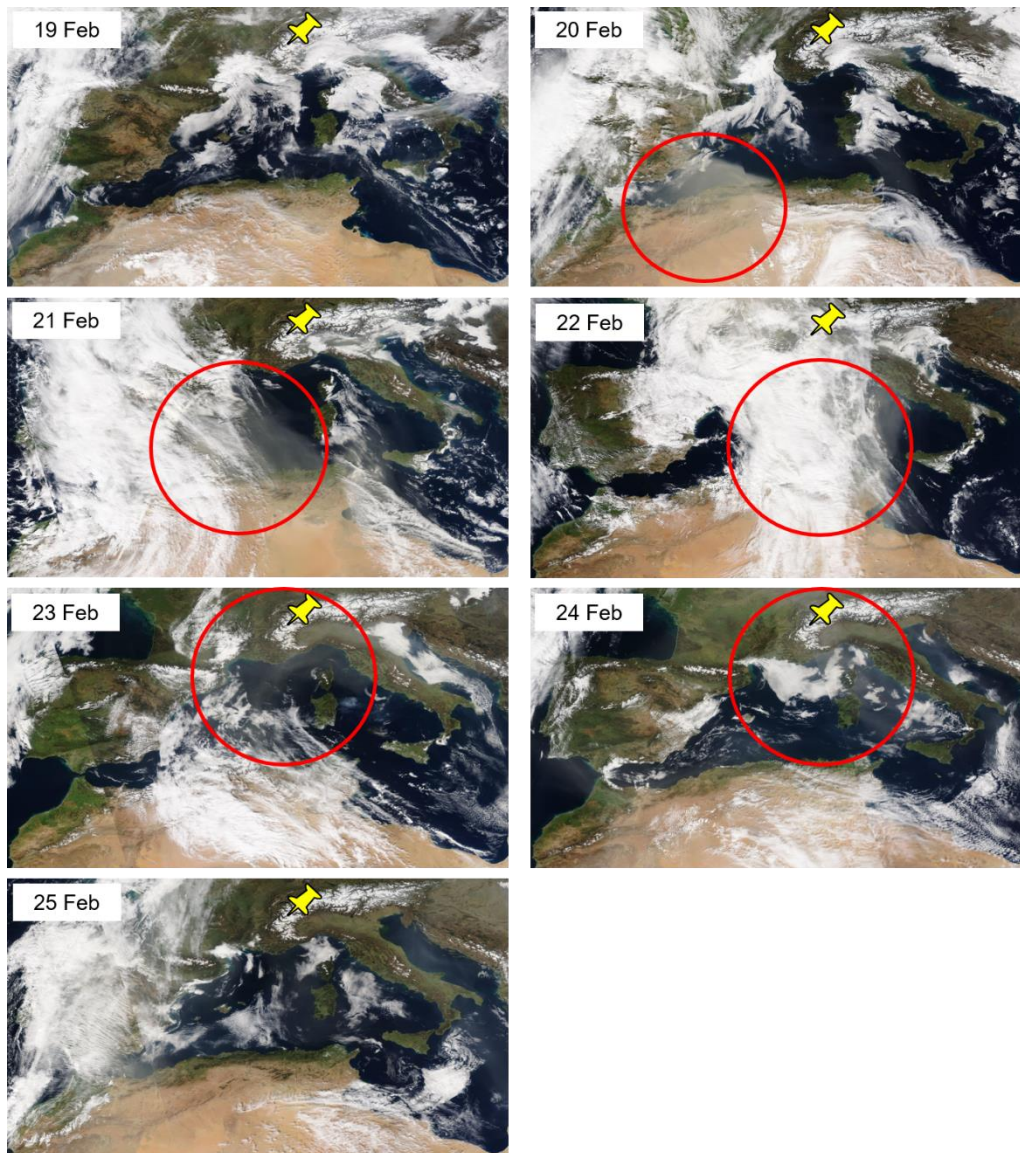
Figure 1. Images from the AQUA satellite (MODIS; © NASA) from 19 February 2021 to 25 February 2021. One can see a plume of Saharan dust forming over North Africa on 20 February (localised by the red circle) and moving above the south of France and the Alps until 24 February. The yellow pin points to Chamonix, France.
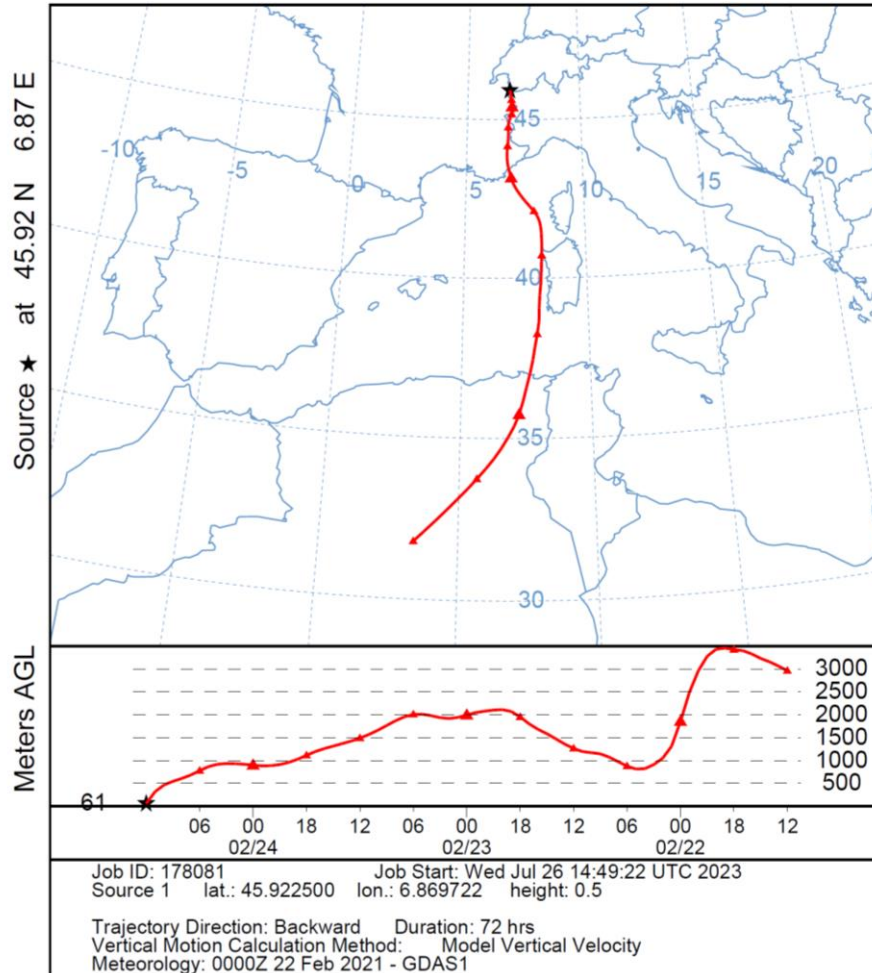
Figure 1. HYSPLIT 72 hours backward trajectory on 24 February 2021 ending at Chamonix, France, at 12:00 UTC (13:00 local time). The model was run every 6 hours. The starting height (in meter above ground level) is half of the boundary layer height estimated by the model from meteorological data set.

Technical comments:

- **Blank correction of isotope measurement of NO₂: I wondered where the blank comes from, if it is coming from the chemicals used to trap NO₂, there is no problem to correct as what was done here; however, if the blank NO₂ was coming from absorption of atmospheric NO₂ during the preparation and the installation of the coated denuder tubes, it won't make sense to do the correction by assuming blank $\Delta^{17}O(NO_2) = 0$ permil, which would over correct.**

Although difficult to assess, it is unlikely that this blank came from atmospheric NO₂ as the denuders of the batches used for SP 1 and SP 2 were handled using the same procedure. It is more likely that this contamination came from the batch of MQ water used to extract the SP 2 denuders or from a contaminated pipette. Since the sample collected between 13:30 and 16:30 LT during SP 2 captured less atmospheric NO₂ than other samples (due to lower ambient NO₂ during this period), the blank has more impact.

- **Equation (4) and relatives in the text: don't get the point why defines a new term T_{NO+O_3} instead of using what has been long used in the literature, i.e., the A value to represent the fraction of O₃ oxidation of NO and this "A" is almost reserved in the study of $\Delta^{17}O$ of nitrate. I suggest to keep consistent with the literature and do not define new terms unless necessary so that peers can easily follow. I understand here the authors used "A*" later to define the lifetime differences, but it can be simply replaced with any other symbols.**

We understand your concern. However, the "*A**" notation was initially used in Albertin et al. (2021) to be consistent with the literature (see Li et al., 2020), so it follows that we could not use this letter for the term relating to T_{NO+O_3}. Thus, for the sake of consistency with Albertin et al. (2021), we would like to keep the term "T_{NO+O_3}". In addition, "*T*" symbolises the word "transfer", a more explicit letter than *A*. Nonetheless, to avoid confusing, we have added in the revised manuscript that this term can also be called *A* in part of the literature.

- **Line 246: These latter, not "later"**

Thank you for pointing this mistake out, which has been corrected.

- **Line 409, I would not call 29.0 +/- 2.2 is consistent with the values of 26 +/- 1 in the literature. In fact, why not just use the relationship of $\Delta^{17}O(O_3{}^*) = 1.5 \times \Delta^{17}O(O_3)_{bulk}$? The latter would derive a lower $\Delta^{17}O(O_3)_{bulk}$ which is more consistent with Vicars and Savarino 2014.**

Regarding the point that we state (29.0 ± 2.2) ‰ to be consistent with the values of (26.2 ± 1.3) ‰, in view of the uncertainty range, this is acceptable in terms of overlapping. However, although our mean value remains consistent with previous studies, we recognise that it is at the lower end of the SD of 29.0 ‰ and at the upper range of the SD of 26 ‰. To support the consistency of our derived $\Delta^{17}O(O_3)_{bulk}$ at (29.0 ± 2.2) ‰ with the study of Vicars and Savarino (2014), we propose to add to the revised manuscript a comparison of our derived $\Delta^{17}O(O_3)_{bulk}$ with the measurements of Vicars and Savarino (2014) performed in February-March. Indeed, it is interesting to note that, over year-round measurements of $\Delta^{17}O(O_3)_{bulk}$ in Grenoble, France (120 km south-west of Chamonix), Vicars and Savarino (2014) reports a large peak of $\Delta^{17}O(O_3)_{bulk}$ values in February-March, 2-3 ‰ greater than the annual mean of (26.2 ± 1.3) ‰. Although the reasons for the higher values at that period remain unknown, our derived $\Delta^{17}O(O_3)_{bulk}$ is surprisingly in very good agreement with the values reported for this period by Vicars and Savarino (2014). We have added this point to the revised manuscript (lines 484-495) as:

"Assuming that their maximum measured daytime $\Delta^{17}O(NO_2)$ reflects the conversion of NO to NO_2 only through Reaction (R3) (i.e., $T_{NO+O_3} = 1$), Albertin et al. (2021) derived a $\Delta^{17}O_{NO+O_3}(NO_2)$ value of 39.2 ‰ from Eq. (3). Given the respective analytical uncertainties (around ±1 ‰), their value is in very good agreement with the maximum daytime value of 40.8 ‰ we observed in Chamonix. Similarly to Albertin et al. (2021), assuming that the highest daytime $\Delta^{17}O(NO_2)$ value at our site corresponds to $T_{NO+O_3} \approx 1$ leads to $\Delta^{17}O_{NO+O_3}(NO_2) = 40.8$ ‰. Using the experimental $\Delta^{17}O_{NO+O_3}(NO_2)$ transfer function determined by Savarino et al. (2008), we estimate a bulk ^{17}O-excess of O_3 ($\Delta^{17}O(O_3)_{bulk}$) at (29.0 ± 2.2) ‰. This value is consistent with the range of direct $\Delta^{17}O(O_3)_{bulk}$ measurements at mid-latitudes (mean of (26.2 ± 1.3) ‰; Vicars and Savarino, 2014), although falling at the upper end of the range. Interestingly, Vicars and Savarino (2014) reported a significant peak in $\Delta^{17}O(O_3)_{bulk}$ during February-March in Grenoble, France (located 120 km southwest of Chamonix), based on year-round measurements with $\Delta^{17}O(O_3)_{bulk}$ values 2–3 ‰ higher than the annual mean of 26.2 ‰. Although the cause of increased values during this period is unknown, our derived $\Delta^{17}O(O_3)_{bulk}$ matches remarkably well the February-March measurements reported by Vicars and Savarino (2014)."

Now, regarding the relationship of $\Delta^{17}O(O_3{}^*) = 1.5 \times \Delta^{17}O(O_3)_{bulk}$, a clarification is needed because there is too much confusion on this, even in published literature. $\Delta^{17}O(O_3{}^*)$ is defined as the $\Delta^{17}O$ bears by the terminal atoms of O_3 (we can also find in the literature $\Delta^{17}O(O_3)_{term}$). It does not represent in any way the actual $\Delta^{17}O$ transfer of O_3 to the species with which it reacts, in our case NO. The relation $\Delta^{17}O(O_3{}^*) = 1.5 \times \Delta^{17}O(O_3)_{bulk}$ is theoretically justified as well as observed in laboratory and follows

that the $\Delta^{17}O$ is only borne by the terminal atoms of O_3. The $\Delta^{17}O$ transfer from O_3 to NO can only be equal to $1.5 \times \Delta^{17}O(O_3)_{bulk}$ if for example NO reacts only with the terminal atoms of O_3. Actually, the work of Savarino et al. (2008) did show that NO does not react only with the O_3 terminal atoms, but also, albeit to a lower extent, with its central atom (probability of (8 ± 5) % for the abstraction of central atoms during the reaction $NO + O_3$). As a result, the $\Delta^{17}O$ transfer of O_3 to NO is slightly lower than $1.5 \times \Delta^{17}O(O_3)_{bulk}$. Therefore, one need to define the term $\Delta^{17}O_{NO+O_3}(NO_2)$ which represents the true $\Delta^{17}O$ transfer during the reactions $NO + O_3$ and this has been quantified by Savarino et al. (2008) with:

$$\Delta^{17}O_{NO+O_3}(NO_2) = (1.18 \pm 0.07) \times \Delta^{17}O(O_3)_{bulk} + (6.6 \pm 1.5) \text{ ‰}$$

Unfortunately, the literature is very heterogeneous in the choice of the $\Delta^{17}O$ transfer functions, mainly due to confusion in the definition of $\Delta^{17}O(O_3^*)$, which is wrongly associated with the transfer of $\Delta^{17}O$ from O_3 to NO. This is why, in the interests of clarification for the community and in order to minimise the uncertainties that can arise from a poor choice of $\Delta^{17}O$ transfer function, we have added few lines on this to our revised manuscript (lines 471-482) as:

"At this point, it is important to recall that the choice of the $\Delta^{17}O_{NO+O_3}(NO_2)$ in Eq. (12) is of a particular importance for quantifying T_{NO+O_3} (as for RO_2). In the literature, $\Delta^{17}O_{NO+O_3}(NO_2)$ varies between 35 ‰ and 41 ‰ (Michalski et al., 2003; Savarino et al., 2016; Vicars et al., 2012; Li et al., 2022; Zhang et al., 2022). This relatively wide range of values is partly a result of some confusion in defining $\Delta^{17}O_{NO+O_3}(NO_2)$, the $\Delta^{17}O$ transfer from O_3 to NO_2. Indeed, the term $\Delta^{17}O(O_3^*)$ is sometimes erroneously used as the transfer function of $\Delta^{17}O$ from O_3 to NO_2 during Reaction (R3). $\Delta^{17}O(O_3^*)$ is actually defined as $\Delta^{17}O$ of O_3 terminal atoms and is also named $\Delta^{17}O(O_3)_{term}$ in the literature. As the $\Delta^{17}O$ in O_3 is borne by its terminal atoms, $\Delta^{17}O(O_3^*) = 1.5 \times \Delta^{17}O(O_3)_{bulk}$. However, $\Delta^{17}O_{NO+O_3}(NO_2)$ can be equal to $1.5 \times \Delta^{17}O(O_3)_{bulk}$ if only terminal atoms of O_3 reacts with NO. But laboratory experiments by Savarino et al. (2008) did show that O_3 does react with NO not solely with its terminal atoms but also, to a small but significant extent, with its central atom (probability of (8 ± 5) % for the abstraction of central atoms during the reaction $NO + O_3$). Consequently, $\Delta^{17}O_{NO+O_3}(NO_2)$ is slightly lower than $1.5 \times \Delta^{17}O(O_3)_{bulk}$ and the $\Delta^{17}O_{NO+O_3}(NO_2)$ expression determined by Savarino et al. (2008) should be used: $\Delta^{17}O_{NO+O_3}(NO_2) = 1.18 \pm 0.07 \times \Delta^{17}O(O_3)_{bulk} + (6.6 \pm 1.5)$ ‰."

- **Line 458: it should be $\Delta^{17}O_{NO_2+O_3}(NO_3)$? Again, if considering terminal O transfer when reacting with O_3, why not simply using the relationship of 1.5? The transfer function $\Delta^{17}O$ from O_3 to NO and NO_2 are different?**

Similarly to our comment above, $\Delta^{17}O_{NO_2+O_3}(NO_3)$ can be associated to $1.5 \times \Delta^{17}O(O_3)_{bulk}$ only if O_3 reacts solely with NO_2 with its terminal atoms. Berhanu et al. (2012) quantified this transfer in the gas phase and found :

$$\Delta^{17}O_{NO_2+O_3}(NO_3) = (1.23 \pm 0.19) \times \Delta^{17}O(O_3)_{bulk} + (9.02 \pm 0.99) \text{ ‰}$$

However, it should be noted that, unlike reaction $NO + O_3$, O_3 do indeed reacts with NO_2 almost entirely with its terminal atoms (see Berhanu et al., 2012 for more details).

References

Albertin, S., Savarino, J., Bekki, S., Barbero, A., and Caillon, N.: Measurement report: Nitrogen isotopes ($\delta^{15}N$) and first quantification of oxygen isotope anomalies ($\Delta^{17}O$, $\delta^{18}O$) in atmospheric nitrogen dioxide, Atmospheric Chemistry and Physics, 21, 10477–10497, https://doi.org/10.5194/acp-21-10477-2021, 2021.

Berhanu, T. A., Savarino, J., Bhattacharya, S. K., and Vicars, W. C.: ^{17}O excess transfer during the $NO_2 + O_3 \rightarrow NO_3 + O_2$ reaction, The Journal of Chemical Physics, 136, 044311, https://doi.org/10.1063/1.3666852, 2012.

Li, Y., Shi, G., Chen, Z., Lan, M., Ding, M., Li, Z., and Hastings, M. G.: Significant Latitudinal Gradient of Nitrate Production in the Marine Atmospheric Boundary Layer of the Northern Hemisphere, Geophysical Research Letters, 49, e2022GL100503, https://doi.org/10.1029/2022GL100503, 2022.

Michalski, G., Scott, Z., Kabiling, M., and Thiemens, M. H.: First measurements and modeling of $\Delta^{17}O$ in atmospheric nitrate., Geophysical Research Letters, 30, 1870, https://doi.org/10.1029/2003GL017015, 2003.

Savarino, J., Bhattacharya, S. K., Morin, S., Baroni, M., and Doussin, J.-F.: The $NO+O_3$ reaction: A triple oxygen isotope perspective on the reaction dynamics and atmospheric implications for the transfer of the ozone isotope anomaly, J. Chem. Phys., 128, 194303, https://doi.org/10.1063/1.2917581, 2008.

Savarino, J., Vicars, W. C., Legrand, M., Preunkert, S., Jourdain, B., Frey, M. M., Kukui, A., Caillon, N., and Roca, J. G.: Oxygen isotope mass balance of atmospheric nitrate at Dome C, East Antarctica, during the OPALE campaign, Atmos. Chem. Phys., 16, 2016.

Vicars, W. C. and Savarino, J.: Quantitative constraints on the ^{17}O-excess ($\Delta^{17}O$) signature of surface ozone: Ambient measurements from 50°N to 50°S using the nitrite-coated filter technique, Geochimica et Cosmochimica Acta, 135, 270–287, https://doi.org/10.1016/j.gca.2014.03.023, 2014.

Vicars, W. C., Bhattacharya, S. K., Erbland, J., and Savarino, J.: Measurement of the 17O-excess ($\Delta17O$) of tropospheric ozone using a nitrite-coated filter, Rapid Communications in Mass Spectrometry, 26, 1219–1231, https://doi.org/10.1002/rcm.6218, 2012.

Zhang, Y.-L., Zhang, W., Fan, M.-Y., Li, J., Fang, H., Cao, F., Lin, Y.-C., Wilkins, B. P., Liu, X., Bao, M., Hong, Y., and Michalski, G.: A diurnal story of $\Delta^{17}O(NO_3^-)$ in urban Nanjing and its implication for nitrate aerosol formation, npj Clim Atmos Sci, 5, 1–10, https://doi.org/10.1038/s41612-022-00273-3, 2022.

Response to the referee #2 (egusphere-2023-744)

Dear anonymous referee,

We thank you for your thorough review of this work and thoughtful comments that greatly improved the readability of the manuscript. Your comments/suggestions are given below in bold, followed by our answers. Changes/new elements added to the manuscript are presented in blue.

General comments:

1) **Two new works that should be digested/interrogated by the authors and incorporated into the work here are listed below. These should provide fodder for discussion of seasonal difference as well as additional datasets that may be more useful to compare with than is currently in the manuscript since this is also a mid-latitude site with significant diurnal variability.**

   Bekker, C., Walters, W.W., Murray, L.T., Hastings, M.G. (2023), Nitrate chemistry in the northeast US part I: nitrogen isotope seasonality tracks nitrate formation chemistry, Atmospheric Chemistry and Physics, 23(7), 4185-420, https://doi.org/10.5194/acp-23-4185-2023.

   Kim, H., Walters, W.W., Bekker, C., Murray, L.T., Hastings, M.G. (2023), Nitrate Chemistry in the Northeast US Part II: Oxygen Isotopes Reveal Differences in Particulate and Gas Phase Formation, Atmospheric Chemistry and Physics, 23(7), 4203-4219, https://doi.org/10.5194/acp-23-4203-2023.

These two publications are now referenced in the manuscript as additional data for comparisons. However, please note that, although these measurements are generally in agreement with our results, these two studies collected nitrate on a weekly basis with gas and particulate phase segregation for nitrate whereas our measurements were performed over 2 days on sub-daily sampling with collection of total nitrate. As a result, the comparison is to some extent limited.

2) **A few aspects related to methodology – evidence needs to be provided that under the conditions in this study that both HNO_3 and particle phase nitrate are quantitively collected. The references cited do not actually prove this, but rather suggest that conditions are alkaline enough that this "should" be true. This can have an important impact as there is large fractionations between the gas and particle phase nitrate. This is ignored in the current study, presumably because of the assumption that total nitrate is collected. But if the particles are decoupled from the gas upon collection, or upon transport, then this could indeed be making a difference in the dataset here. This topic should be better addressed in the manuscript (see general comments below tied to line/section numbers). See for instance Geng et al. (2017) treatment of this (this work is already cited in manuscript) and Li et al. (2020) (citation below).**

Regardless of the type of filter substrate, determining the exact nature of the nitrate collected on filter samples has always been a matter of debate, and no medium can completely prevent sampling artefacts

(e.g., Schaap et al., 2002; Appel et al., 1980). For instance, nitric acid (HNO_3) can potentially be absorbed on aerosols that have already deposited on the filter material. In addition, HNO_3 can evaporate from the filter after exposure. We recognise that the references cited do not prove that glass fibre filters effectively collect both HNO_3 and particulate nitrate (p-NO_3^-), but only assume that the ambient conditions (i.e., marine boundary layer and therefore the presence of sea salts) allow effective collection of HNO_3, as has already been discussed in the literature (e.g., Prospero and Savoie, 1989). In our case, and we agree that this should be mentioned more explicitly, since the ambient air in Chamonix is likely free of sea salts, we did not pre-wash the glass fibre filters before using them. In fact, they are already highly loaded with NaCl due to their manufacturing process. Therefore, we assume that HNO_3 is collected quantitatively on the glass fibre filters due to their NaCl coating, which has been shown in the literature to collect HNO_3 (Appel et al., 1981). If you with, we can share the IC analyses of virgin filters, which prove the high NaCl loading.

However, although we cannot cite any published study that proves the efficiency of HNO_3 collection using GF filters, we would like to share here our own investigation into this topic which provides some support. Figure 1 below shows a comparison of nitrate concentrations obtained from collections on GF filters using two high-volume samplers installed in parallel at the Concordia station on the Antarctic plateau. One of the samplers was equipped with GF filters without any pre-treatment, while the second used NaCl-coated GF filters. It can be seen that there is almost no difference between the two type of filters. Furthermore, at Concordia, nitrates are mostly present under HNO_3 in summer, reaching around 100 ng m^{-3}, which is 10 times higher than the p-NO_3^- concentration (Legrand et al., 2017). As our nitrate concentrations also reach around 100 ng m^{-3} in summer, this means that we are necessarily effectively collecting HNO_3. In addition, Figure 2 shows a comparison of nitrate collection at Concordia with two different filter types, GF and cotton (Whatman® 41). Clearly, it appears again that the GF collected more than 100 ng m^{-3} of nitrate in summer, in agreement with Legrand et al. (2017), whereas cotton filters collected much less nitrate, probably corresponding to the particulate phase only. Finally, Figure 3 shows a comparison of nitrate collections at Concordia with coated denuder tubes (collecting only the gas phase), Teflon, and GF filters. Please note that the sampling steps are not the same between the different sampling media. However, it is clearly visible that the HNO_3 concentrations collected by the denuders are in good agreement with the GF collections, while the Teflon filters show much lower nitrate concentrations, suggesting that only the particulate phase was collected.

Figure 1. Comparison of filter collection efficiency for atmospheric nitrate sampling at Concordia, Antarctica. The black triangles represent concentration of nitrate collected with glass fiber filters without any pre-treatments and the red squares represent concentration of nitrate collected with glass fibre filter coated with NaCl. Data courtesy : Joël Savarino, unpublished data.

Figure 2. Comparison of filter collection efficiency for atmospheric nitrate sampling at Concordia, Antarctica. The blue triangles represent concentration of nitrate in ng m^{-3} collected with glass fiber filters without any pre-treatments and the orange squares represent concentration of nitrate collected with cotton filter. Data courtesy : Joël Savarino, unpublished data.
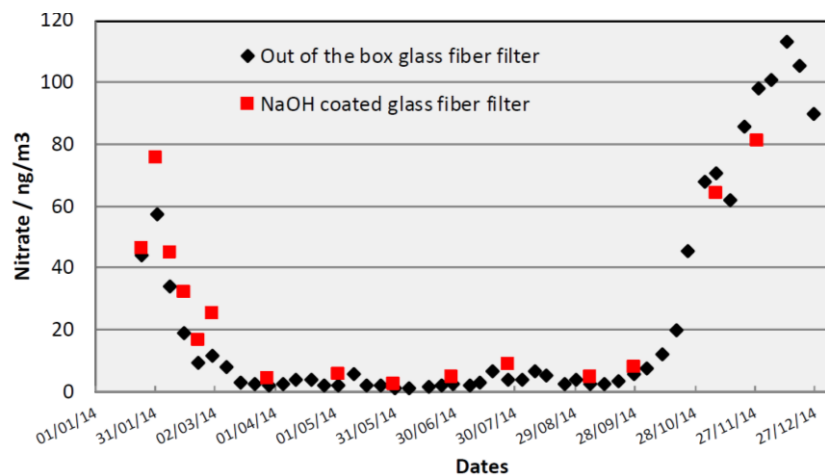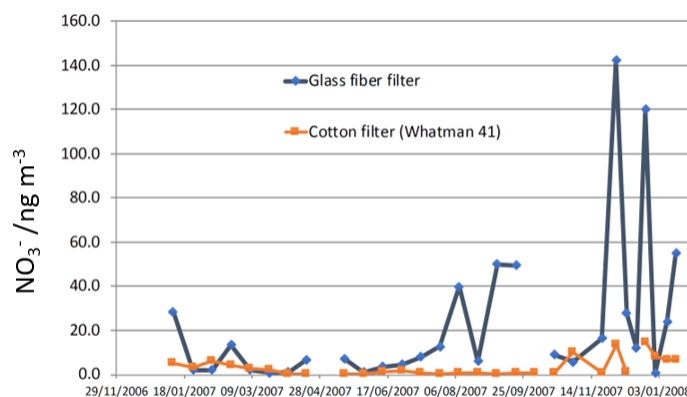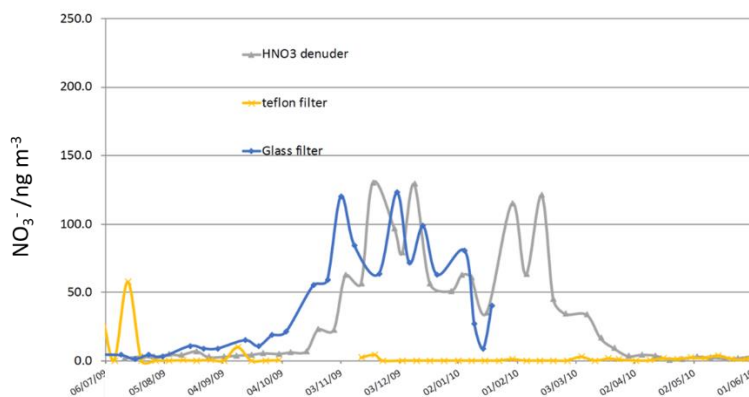
Figure 3. Comparison of filter collection efficiency for atmospheric nitrate sampling at Concordia, Antarctica. The blue triangles represent concentration of nitrate collected with glass fiber filters without any pre-treatments, the grey triangles represent concentration of nitrate collected with coated denuders, and the yellow crosses represent concentration of nitrate collected with Teflon filter. Data courtesy : Joël Savarino and Michel Legrand, unpublished data.

We have added a few lines in the revised manuscript to better explain our approach (lines 184-193):

"Evaluating the collection efficiency of total NO_3^- has long been debated (e.g., Schaap et al., 2002; Appel et al., 1980) and, although not free from sampling artefacts (e.g., potential volatilisation of HNO_3 after exposure to ambient air), GF filters have been used on several times to study nitrate isotopes, mainly in coastal sites (e.g., Savarino et al., 2007; Michalski et al., 2003; Morin et al., 2009; Frey et al., 2009; Morin et al., 2007a; Patris et al., 2007; Vicars et al., 2013). Under these conditions, the aerosol alkalinity is supposed to allow the collection of HNO_3 (Prospero and Savoie, 1989). In our case, as the ambient air in Chamonix is expected to be free of sea salt, the GF filters were not washed before use in order to keep the initial NaCl coating inherited from the filter manufacturing process. Therefore, in addition to p-NO_3^-, we are confident that the high GF filter NaCl loading allowed the quantitative collection of HNO_3 at our site, as it has been shown previously in the literature (Appel et al., 1981; see also our reply and data to the comments of Reviewer #2 on this specific issue)."

With regard to your concern on the distribution of NO_3^- between the gaseous phase (HNO_3) and/or aerosols phase (p-NO_3^-) during transport, the studies you cite were carried out in remote regions (Greenland and the Tibetan Plateau) and are based on NO_3^- analysed in ice cores. The problematic is therefore different, in particular because our sampling site is much closer to the emission sources than these two sites. Numerous studies have shown the dominant influence of local pollution in our sampling area (e.g., Chazette et al., 2005; Quimbayo-Duarte et al., 2021; Allard, 2018; Chevrier, 2016). In consequence, most of the NO_3^- at our site is most likely formed locally, i.e., in the vicinity of Chamonix and/or in a surrounding area of a few tens of kilometres. The residence time of NO_3^- in the atmosphere before being sampled at our site is much shorter than that analysed in Greenland and Tibetan Plateau ice cores, and we can therefore expect post-NO_3^- portioning to be negligible, all the more so if we

consider our sampling steps at high temporal resolution (typically 3 h). However, although probably minor in winter due to high local NO_x emissions and poor dispersion due to the low height of the surface boundary layer and surrounding high-altitude mountains, we acknowledge the possibility of an influence of NO_3^- input through long range transport, as it could be the case during SP 2 due to Saharan dust entering the Chamonix valley. In such circumstances, we agree that the distribution between the gas and the particulate phase may be affected due to the promotion of HNO_3 dry scavenging by dust and/or heterogeneous processes at the aerosol surface, both of which may have an impact on the isotopic distribution of NO_3^- collected at the surface. This influence of a change in NO_3^- origins on its O and N isotopic composition during SP 2 is discussed in the manuscript.

3) **Also, how is it ensured that there is no exchange of water with the analyte nitrite (ie NO_2)? And are the oxygen isotopes scaled to the nitrate reference materials or only the nitrite reference materials? Exchange is relatively fast for nitrite in solution (even in frozen solutions) and has been the subject of corrections and difficulties in several studies (see for instance Casciotti and McIlvin, 2007; Wankel et al. 2009).**

Casciotti, K. and M. McIlvin (2007), Isotopic analyses of nitrate and nitrite from reference mixtures and application to Eastern Tropical North Pacific waters, Marine Chemistry, 107(2), 184-201, https://doi.org/10.1016/j.marchem.2007.06.021.

Li, Z., M.G. Hastings, W.W. Walters, L. Tian, S.C. Clemens, L. Song, L. Shao, Y. Fang (2020), Isotopic evidence that recent agriculture overprints climate variability in nitrogen deposition to the Tibetan Plateau, Environment International, 138, https://doi.org/10.1016/j.envint.2020.105614.

Wankel, S.D., et al., (2009) Sources of aerosol nitrate to the Gulf of Aqaba: Evidence from d^{15}N and d^{18}O of nitrate and trace metal chemistry, Marine Chemistry, doi:10.1016/j.marchem.2009.01.013.

The integrity of the isotopic composition of NO_2^- has already been extensively tested in the cited reference (Albertin et al., 2021). Furthermore, prior to Albertin et al. (2021), Walters et al. (2018) also validated this analytical procedure for O isotopic analysis of NO_2^-. In short, matrix alkalinity limits O isotopic exchanges between NO_2^- and water to some extent. For more details on our study of the stability of the NO_2^- isotopic composition, we invite you to read section 2.2 of Albertin et al. (2021) and its Appendix B which demonstrates the stability of the O isotopic composition of NO_2^- isotopic reference materials over several weeks. Please note that we were also able to control O isotopic exchange by preparing several nitrite standards enriched in ^{17}O (unpublished data currently being analysed for intercomparison purposes).

The N and O isotopes of NO_2^- analytes are only scaled relative to the NO_2^- reference materials (see the detailed calibration procedure in Albertin et al., 2021). The isotopic composition of NO_3^- cannot be measured with the azide method because it does not convert NO_3^- to N_2O, but only to NO_2^-. We chose to carry out a calibration based on NO_2^- standards, assuming conservation of $\Delta^{17}O$. If NO_3^- were used, this would require a reduction step to NO_2^- on activated cadmium, a process that is difficult to reproduce under equivalent conditions and during which we cannot certify the conservation of $\Delta^{17}O$.

4) **The crux of the interpretation and conclusion rely on NO_2 having a short lifetime such that production of nitrate from NO_2 is controlled by local chemistry. The lifetime of NO_2 photolysis is calculated, but the lifetime of NO_2 loss (as nitrate) is not. The calculation of $\Delta^{17}O$-nitrate relies on $\Delta^{17}O(NO_2)$. At each time step (3 h interval) the nitrate is calculated from the NO_2. A weighted average of the $\Delta^{17}O$-NO_3^- values is then taken and compared to the daytime average after the first 3 h interval. This 3 h offset is suggested to take care of the time to convert NO_2 to nitrate. The weighting of each 3 h interval for NO_3^- is based on $[NO_2]*J_{NO_2}$ as a proxy for OH production. These values also represent a time when NO_2 is being photolyzed, not converted by OH to nitrate. When the nitrate $\Delta^{17}O$ calculated values match with the observations it is taken as proof that the short lifetime is robust. When they do not agree, there has to be another (non-local) source of nitrate. But the authors started with the assumption that at each time interval the $\Delta^{17}O$-NO_2 is relevant to the $\Delta^{17}O$-NO_3^- collected. This all ends up a bit messy (albeit complex). It seems that it might make more sense to calculate an average (weighted) daytime $\Delta^{17}O$-NO_2 and then calculate an average $\Delta^{17}O$-NO_3^- from this weighted NO_2. There is not a direct link between the simultaneously collected NO_2 and NO_3^- - in other words, the NO_3^- collected in that time interval cannot be from the NO_2 that was also collected in that time interval. So really what can be tested is whether there is diurnal variability in the signals and then for the comparison purposes use the average $\Delta^{17}O$-NO_2 to predict average NO_3^- and see how that compares with the observations. If the authors disagree, then the approach they are currently taking needs to be better justified.**

The time lag was intended to take account of the time required to convert NO_2 in to HNO_3. We agree that this 3 hr shift seems somewhat arbitrary. Following your comment, we have revised our methodology. In the revised version of the manuscript, we average the daytime observations of $\Delta^{17}O(NO_2)$ between 7:30 and 18:00 LT, which are now compared with observed $\Delta^{17}O(NO_3^-)$ averaged over the same period. At night, we average observed $\Delta^{17}O(NO_2)$ and $\Delta^{17}O(NO_3^-)$ between 18:00 and 7:30 LT. Although the mean values are different compared with the initial version of the manuscript, the general conclusions do not change because the difference between calculated and observed $\Delta^{17}O(NO_3^-)$ is still greater during SP 2 than during SP 1. We have also modified the average period for $\delta^{15}(NO_2)$ and $\delta^{15}(NO_3^-)$ and in a same way, despite the changes in the average values, the general conclusions are similar to the initial version, showing a distinctive behaviour of the N isotopes of NO_3^-

during SP 2. As a result, Table 2 and 4 have been updated in the revised manuscript with the new values as:

		$\Delta^{17}O(NO_2)$ /‰	$\Delta^{17}O(NO_3^-)$ /‰	$\Delta^{17}O_{calc}(NO_3^-)$ /‰	$\Delta^{17}(NO_3^-_{calc} - NO_3^-_{obs})$
Daytime	SP 1	30.0 ± 7.3	23.0 ± 3.1	22.5 ± 4.6	-0.5
(7:30-18:00)	SP 2	26.1 ± 6.9	23.9 ± 3.8	17.5 ± 4.6	-6.4
Nighttime	SP 1	21.2 ± 1.1	20.5 ± 1.1	21.4 ± 0.7	0.9
(18:00-7:30)	SP 2	20.8 ± 1.0	23.2 ± 1.0	21.0 ± 0.6	-2.2

Table 2. Mean observed $\Delta^{17}O$ data of NO_2 ($\Delta^{17}O(NO_2)$) and NO_3^- ($\Delta^{17}O(NO_3^-)$) in Chamonix, and mean calculated $\Delta^{17}O$ of NO_3^- ($\Delta^{17}O_{calc}(NO_3^-)$) using Eqs. (6) and (7) at day and night, respectively, constrained with observed $\Delta^{17}O(NO_2)$. Day and night calculated values were weighted by $[NO_2] \times J_{NO_2}$ and $[NO_2] \times [O_3]$, respectively

		$\delta^{15}N(NO_2)$ /‰	$\delta^{15}N(NO_3^-)$ /‰	$\delta^{15}N(NO_x)$ /‰	$\delta^{15}N(NO_3^- - NO_2)$ /‰
Daytime	SP 1	7.4 ± 4.7	7.0 ± 6.7	-9.9 ± 2.9	-0.4
(7:30-18:00)	SP 2	14.0 ± 13.9	4.0 ± 6.4	-10.8 ± 2.1	-10.0
Nighttime	SP 1	-5.1 ± 2.3	1.4 ± 1.2	-9.0 ± 0.8	6.3
(18:00-7:30)	SP 2	-2.5 ± 4.2	-1.1 ± 0.4	-9.9 ± 1.9	1.4

Table 4. Mean observed $\delta^{15}N$ data of NO_2 ($\delta^{15}N(NO_2)$) and NO_3^- ($\delta^{15}N(NO_3^-)$), calculated atmospheric $\delta^{15}N$ of NO_x ($\delta^{15}N(NO_x)$, and $\delta^{15}N$ shift between $\delta^{15}N(NO_3^-)$ and $\delta^{15}N(NO_2)$ ($\Delta^{15}(NO_3^- - NO_2)$).

These new values has been inserted in the revised manuscript in sections describing these data as (lines 518-560):

"To investigate the factors influencing the variability of $\Delta^{17}O(NO_3^-)$ at our site, one compare observed $\Delta^{17}O(NO_3^-)$ with estimated values of $\Delta^{17}O(NO_3^-)$ derived from $\Delta^{17}O$ mass balance and observed $\Delta^{17}O(NO_2)$, assuming the OH and N_2O_5 pathways dominate the formation of NO_3^- at our site. Therefore, calculated $\Delta^{17}O(NO_3^-)$ reflect the theoretical $\Delta^{17}O$ transfer during the oxidation of NO_2 to NO_3^- at our site through the dominant chemical process during the day (i.e. OH pathway) and at night (i.e. N_2O_5 pathway).

As presented, during the day, we consider that the conversion of NO_2 into NO_3^- is predominantly influenced by Reaction (R5) (OH pathway). Hence, the theoretical corresponding ^{17}O-excess transfer to NO_3^- is estimated using Eq. (6) and observed $\Delta^{17}O(NO_2)$ between 7:30 and 18:00 LT (n = 3 per sampling period). Then, in order to estimate a daytime average value of $\Delta^{17}O(NO_3^-)$ which is representative of the potential for the formation of NO_3^- from surface NO_2 by the OH pathway, each calculated $\Delta^{17}O(NO_3^-)$ is weighted by the product $[NO_2] \times J_{NO_2}$ (the diurnal variability of the OH mixing ratio is assumed to follow the diurnal J_{NO_2} variation; Liu et al., 2021). Finally,

an overall mean daytime $\Delta^{17}O(NO_3^-)$ for SP 1 and SP 2 is estimated by taking the sum of the weighted calculated values ($=\Delta^{17}O_{calc}(NO_3^-)$). The same approach is used during the night, assuming that the conversion of NO_2 into NO_3^- is dominated by Reactions (R6)−(R8) (N_2O_5 pathway). Eq.(7) and observed $\Delta^{17}O(NO_2)$ between 18:00 and 7:30 LT (n = 3 per sampling day) are used to estimate $\Delta^{17}O(NO_3^-)$. Each calculated $\Delta^{17}O(NO_3^-)$ is weighted by the product $[NO_2]\times[O_3]$ (i.e., NO_3 production rate) and summed to estimate a mean nighttime $\Delta^{17}O(NO_3^-)$ for SP 1 and SP 2. The ^{17}O-excess transferred from O_3 to NO_2 during Reaction (R6) ($\Delta^{17}O_{NO_2+O_3}(NO_3)$) is fixed at 44.7 ‰. This value is set accordingly to the transfer function reported by Berhanu et al. (2012) whereby $\Delta^{17}O_{NO_2+O_3}(NO_3) = (1.23 \pm 0.19) \times \Delta^{17}O(O_3)_{bulk} + (9.02 \pm 0.99)$ and $\Delta^{17}O(O_3)_{bulk} = 29.0$ ‰ (see Section 2.4.1). We compare hereafter $\Delta^{17}O_{calc}(NO_3^-)$ with the weighted day and night averages of observed $\Delta^{17}O(NO_3^-)$ at our site. During the day, $\Delta^{17}O_{calc}(NO_3^-)$ is compared with $\Delta^{17}O(NO_3^-)$ observations averaged between 7:30 and 18:30 LT (n = 3). At night, $\Delta^{17}O_{calc}(NO_3^-)$ is compared with $\Delta^{17}O(NO_3^-)$ observations averaged between 18:30 to 7:30 LT.

At night during SP 1, observed $\Delta^{17}O(NO_3^-)$ and $\Delta^{17}O_{calc}(NO_3^-)$ are in good agreement ($\Delta^{17}O_{calc}(NO_3^-)$ − $\Delta^{17}O(NO_3^-)$ = $\Delta^{17}(NO_3^-{}_{calc} - NO_3^-{}_{obs})$ = 0.9 ‰), suggesting a local and rapid (< 12 h) conversion of NO_2 into NO_3^- via the N_2O_5 pathway. During the day, observed $\Delta^{17}O(NO_3^-)$ is 0.5 ‰ higher than $\Delta^{17}O_{calc}(NO_3^-)$, also suggesting that NO_3^- is formed locally during the day for oxidation of surface NO_2 through the OH pathway. Small differences between observed and calculated $\Delta^{17}O$ of NO_3^- during the day/night could be explained by the presence of NO_3^- residues formed during the previous night/day, which are not considered in the calculations since they do not account for NO_3^- lifetime. In contrast to SP 1, $\Delta^{17}O_{calc}(NO_3^-)$ during SP 2 is significantly lower than the mean observed $\Delta^{17}O(NO_3^-)$, particularly during the day with a $\Delta^{17}(NO_3^-{}_{calc} - NO_3^-{}_{obs})$ of −6.4 ‰. The significant gap between observed and calculated $\Delta^{17}O(NO_3^-)$ suggests a different origin and/or formation process of NO_3^- during SP 2 compared to SP 1. Although less important than during the day, $\Delta^{17}O_{calc}(NO_3^-)$ values for SP 2 at night is lower by 2.2 ‰ to the observed value. This small shift can be explained by residuals of enriched daytime NO_3^-. It is important to point out that, although the NO_2 sample collected on Feb 24 between 13:30 and 16:30 LT presents an important blank (ca. 14 %), ambient NO_2 is low during the sampling period (mean of (4.5 ± 1.8) nmol mol^{-1}). Therefore, as each $\Delta^{17}O$ value used to estimate $\Delta^{17}O_{calc}(NO_3^-)$ is weighted by the mean ambient NO_2 mixing ratio over the sampling period, the incertitude related to this blank has little influence on the daily average of $\Delta^{17}O_{calc}(NO_3^-)$. Given the low $\Delta^{17}(NO_3^-{}_{calc} - NO_3^-{}_{obs})$ during SP 1, observed $\Delta^{17}O(NO_3^-)$ can be explained by the local and rapid (< 12 h) oxidation of NO_2, dominated by the OH and N_2O_5 pathway during the day and night, respectively. However, in contrast to SP 1, the ^{17}O-excess measured in NO_3^- during the day of SP 2 cannot be fully constrained by the oxidation of surface NO_2 through the OH pathway, suggesting that the formation mechanisms of NO_3^- are different between SP 1 and SP 2 and/or the presence of NO_3^- not formed locally during SP 2. Below we examine the changes in the sub-daily dynamics of $\Delta^{17}O(NO_3^-)$ between SP 1 and SP 2 in light of atmospheric observations."

and as (lines 726-760):

"$\delta^{15}N(NO_3^-)$ also exhibits substantial variability during the day, ranging from −1.3 ‰ to 14.9 ‰ and from −4.2 ‰ to 9.7 ‰ during SP 1 and SP 2, respectively. At night, $\delta^{15}N(NO_3^-)$ is less variable, with an overall mean of (1.4 ± 1.2) ‰ and (−1.1 ± 0.4) ‰ during SP 1 and SP 2, respectively. $\delta^{15}N(NO_3^-)$ is within the range of observations reported in urban areas (He et al., 2020; Zhang et al., 2022). A similar diurnal pattern was observed in samples collected during a cruise along the Californian coast in spring 2010 (Vicars et al., 2013), and isotopic exchanges between NO and NO_2 during the day were found to be the primary driver of the diel variability. In the previous section, we demonstrated that there is a significant ^{15}N partitioning between NO_x emissions and NO_2, the latter being enriched in ^{15}N compared to NO_x emissions. Interestingly, important enrichments in ^{15}N are also observed in NO_3^-.

As described above, at night during SP 1 and SP 2, $\delta^{15}N(NO_2)$ is close to $\delta^{15}N(NO_x)$ due to small N fractionation effects. However, between 18:00−7:30 LT, NO_3^- is enriched in ^{15}N relative to NO_2 by +6.3 ‰ and +1.4 ‰ in average during SP 1 and SP 2, respectively (Table 4). If we assume that, at night, NO_3^- is formed mainly by the conversion of surface NO_2 via the N_2O_5 pathway, then the difference between $\delta^{15}N(NO_3^-)$ and $\delta^{15}N(NO_2)$ ($\Delta^{15}(NO_3^- - NO_2)$) should reflect the N enrichment factor associated to this oxidation process. It is likely that an isotopic equilibrium is established between NO_2, NO_3, and N_2O_5, hence affecting the partitioning of ^{15}N between NO_2 and NO_3^- produced at night (Walters and Michalski, 2016). Neglecting KIE associated with the N_2O_5 pathway and using the expression of the EIE fractionation factor between N_2O_5 and NO_2 given by Walters and Michalski (2015) (Appendix D) constrained with the mean nighttime temperature at our site, the isotopic composition of NO_3^- is expected be enriched in ^{15}N by about 29 ‰ compared to NO_2. This estimated ^{15}N enrichment is about three times higher than the observed $\Delta^{15}(NO_3^- - NO_2)$ at our site. As daytime NO_3^- exhibits higher $\delta^{15}N$ values than during the night, it is not possible for daytime residuals at night to account for the lower than predicted fractionation effect between NO_2 and NO_3^-. These results highlight the importance of improving our understanding of the ^{15}N fractionation between NO_2 and NO_3^- associated with the N_2O_5 pathway. This could be achieved in an atmospheric simulation chamber that allows to reproduce individual processes in controlled conditions. The ^{15}N isotopic enrichment of NO_2 and NO_3^- collected from 7:30 to 18:00 LT shows a very contrasted distribution between SP 1 and SP 2, with a respective average $\Delta^{15}(NO_3^- - NO_2)$ of −0.4 ‰ and −10.0 ‰ (Table 4). Although subjected to significant uncertainties (Fan et al., 2019), the OH pathway is often associated to a KIE effect of −3 ‰ (Freyer, 1991), which is at odds with our observations. Similarly to the N_2O_5 pathway, there is an important need to better estimate the fractionation factor associated with the OH pathway.

There are significant differences in $\Delta^{15}(NO_3^- - NO_2)$ between SP 1 and SP 2, providing further evidence that NO_3^- collected during these two periods has undergone different formation processes and/or originate from different sources of NO_2. In addition, possible fractionation associated with phase change between HNO_3 and p-NO_3 during transport of Saharan dust could influence the $\delta^{15}N$ of collected NO_3^- during SP 2. However, given the lack of knowledge about N fractionation factors between NO_2 and NO_3^- and our limited dataset, we cannot conclude whether the changes in the distribution of NO_3^- isotopes during SP 2 result from changes in the phase distribution of NO_3^- or in NO_2 oxidation processes."

In hindsight, a key aspect to consider when comparing calculated and observed $\Delta^{17}O(NO_3^-)$ is not actually the timescale for conversion of NO_2 into NO_3^-, but rather the residence time of NO_3^-, which is determined by deposition. Indeed, if NO_3^- residence time was significantly shorter than the averaging period of $\Delta^{17}O(NO_2)$ and $\Delta^{17}O(NO_3^-)$, most of the NO_3^- sampled during a specific averaging period would originate from NO_2 oxidised during the same period. Reversely, if NO_3^- residence time was much longer than the averaging period, most of NO_3^- sampled during a specific averaging period would come from NO_2 from previous averaging periods. Here, NO_3^- residence time against dry deposition is estimated to reach a maximum of 28 h when the boundary layer (BL) is at 500 m, and 6 h when the BL is at 100 m. These two altitudes are considered respectively as the maximum daytime and minimum nighttime altitudes of the BL at our sampling site. Therefore, most of nocturnal NO_3^- is expected to reflect nocturnal oxidation of NO_2, especially towards the end of the night. During the day, NO_3^- is more likely to reflect both daily oxidation of NO_2 and nocturnal NO_3^- because residues of nocturnal NO_3^- present after sunrise should persist longer during the day than during the night.

5) **The presence and photolysis of HONO is used in the discussion of the oxygen isotopes to infer a major source of RO_2 radicals in wintertime. HONO, however, is not brought at all into the interpretation of the $\delta^{15}N$. Both the $\delta^{15}N$ and $\delta^{18}O$ are impacted by the oxidation processes because of the fractionations detailed by the authors. So an explanation for one isotope necessarily impacts the interpretation of the other when that species can also be source of N.**

Although the photolysis of HONO can indeed be considered as a source of OH radicals at our site at this time of the year, given the high flux of direct NO_x emissions from anthropogenic sources, it is unlikely that the production of NO by HONO photolysis would have a significant impact on the $\delta^{15}N$ of NO_2 and NO_3^-. First, HONO is generally below or in the order of ppb (e.g., Michoud et al., 2014), which is important for OH production in winter but is negligible compared to NO_x levels of a few tens of ppb observed at our site. Secondly, HONO production has been estimated during field campaigns at different sites, for instance 3 ppb h^{-1} in Tai'an (Xue et al., 2022), 2.6 ppb h^{-1} in Beijing (Spataro et al., 2013), 0.7 ppb h^{-1} in Paris (Michoud et al., 2014), and 1.77 ppb h^{-1} in Santiago (Elshorbany et al., 2009). All these references are cited in Ye et al. (2023). Based on these estimates, the HONO production rate cannot compete with the NO-NO_2 conversion/recycling rates in our case. Thirdly, it is clear from data described in Section 3.4.1 that N isotopic equilibrium effects between NO and NO_2 drive the main variability of $\delta^{15}N$ at our site.

Major comments:

Abstract

- **Lines 17, 23-24: add n= # of samples when reporting on the deltas measured**

Thank you for pointing this out, this information has been added to the revised manuscript. Besides, the abstract has been slightly reworded to ease the reading as:

"The oxygen ($\Delta^{17}O$) and nitrogen ($\delta^{15}N$) isotopic compositions of atmospheric nitrate (NO_3^-) are widely used as tracers of its formation pathways, precursor (nitrogen oxides (NO_x) ≡ nitric oxide (NO) + nitrogen dioxide (NO_2)) emission sources, and physico-chemical processing. However, the lack of observations on the multi-isotopic composition of NO_2 maintains significant uncertainties regarding the quantitative links between the isotopic composition of NO_x and NO_3^-, which ultimately may bias inferences on NO_3^- formation processes and distribution of sources, particularly in winter urban atmospheres. We report here on the first simultaneous atmospheric observations of $\Delta^{17}O$ and $\delta^{15}N$ in NO_2 (n = 16) and NO_3^- (n = 14). The measurements were carried out at sub-daily (~ 3 h) resolution over two non-consecutive days in an Alpine city in February 2021. A strong diurnal signal is observed in both NO_2 and NO_3^- multi-isotopic composition. $\Delta^{17}O$ of NO_2 and NO_3^- ranges from 19.6 ‰ to 40.8 ‰ and from 18.3 ‰ to 28.1 ‰, respectively. During the day and night, the variability of $\Delta^{17}O(NO_2)$ is mainly driven by the oxidation of NO by ozone, with a substantial contribution from peroxy radicals in the morning. NO_3^- mass balance equations, constrained by observed $\Delta^{17}O(NO_2)$, suggest that during the first day of sampling, most of NO_3^- was formed locally from the oxidation of NO_2 by hydroxyl radicals by day, and via heterogeneous hydrolysis of dinitrogen pentoxide at night. For the second day, calculated and observed $\Delta^{17}O(NO_3^-)$ do not match, particularly daytime values; the possible effects on $\Delta^{17}O(NO_3^-)$ of a Saharan dust event that occurred during this sampling period and of winter boundary layer dynamics are discussed. $\delta^{15}N$ of NO_2 and NO_3^- ranges from −10.0 ‰ to 19.7 ‰ and from −4.2 ‰ to 14.9 ‰, respectively. Consistent with theoretical predictions of N isotope fractionation, the observed variability of $\delta^{15}N(NO_2)$ is explained by significant post-emission equilibrium N fractionation. After accounting for this effect, vehicle exhaust is found to be the primary source of NO_x emissions at the sampling site. $\delta^{15}N(NO_3^-)$ is closely linked to $\delta^{15}N(NO_2)$ variability, bringing further support to relatively fast and local NO_x processing. Uncertainties on current N fractionation factors during NO_2 to NO_3^- conversion are underlined. Overall, this detailed investigation highlights the potential and necessity to use simultaneously $\Delta^{17}O$ and $\delta^{15}N$ in NO_2 and NO_3^- in order to better constrain quantitative inferences on the sources and formation chemistry of NO_3^- in urban environments in winter."

- **Lines 16 and 24-25: the meaning of "important diurnal variabilities is unclear, please rephrase to be quantitative or use a better description than just "important"**

12

We agree that the terms were not appropriate. In the revised manuscript, line 16 has been rephrased with "A strong diurnal signal is observed …" and line 24-35 with " … the observed variability of …" (see our response above for the full abstract).

- **Line 19: rephrase "NO$_3^-$ local mass balance equations"**

The term "local" has been removed in the revised manuscript.

- **Line 30: "particularly in urban environments in winter" – measurements represent winter only**

The term "particularly" has been removed in the revised manuscript.

Introduction:

The introduction well covers most of the important literature on the topic, but is really too expansive for the purposes of this case study. The introduction should focus on atmospheric chemistry in urban regions under the conditions in this study. It would also be useful to refer directly to the reactions as they are being described to keep readers following the text and the series of reactions. All of the chemistry presented as "the important reactions" are based on global studies and may not be representative of chemistry in urban areas. It should also be noted that only one of the reactions includes a phase (e.g., HNO$_3$(g)) and this should be made more consistent throughout the reactions. Furthermore, the titration of ozone should be explicitly discussed in the introduction as this is a major aspect of the nighttime chemistry in regions where there are continuous, fresh NO emissions at night (i.e., urban areas).

The introduction has been modified/reworded in the revised manuscript accordingly as (line 33-171):

"Despite extensive efforts in emission controls in recent decades, global anthropogenic emissions of nitrogen oxides (NO$_x$ $\equiv$ nitrogen monoxide (NO) + nitrogen dioxide (NO$_2$)) remain more than two orders of magnitude higher than before the Industrial Revolution (Hoesly et al., 2018). Atmospheric nitrate (NO$_3^-$ $\equiv$ nitric acid (HNO$_3$) + particulate nitrate (p-NO$_3^-$)), is the main end-product of NO$_x$ oxidation and a key component of fine particulate matter (PM), which adversely affects human health (WHO, 2021) and contributes to climate change (Masson-Delmotte et al., 2021). NO$_3^-$ can be transported far from emission sources and can be removed from the atmosphere through dry and wet deposition within hours to days (Alexander et al., 2020; Park et al., 2004). The additional input of this "reactive" nitrogen (N$_r$) into natural environments is known to have detrimental consequences, particularly regarding biodiversity and water quality (Galloway et al., 2008; Vitousek et al., 1997). It is therefore

important to have a comprehensive understanding of NO_x emission sources and oxidation processes, on which effective air quality and climate change mitigation strategies rely (e.g., Bauer et al., 2007; Huang et al., 2014; Shah et al., 2018; Tsimpidi et al., 2008; Wang et al., 2013, 2020).

Several studies noted that the response of NO_3^- concentration in air to NO_x emission reduction is contrasted, particularly in winter (e.g., Shah et al., 2018; Tørseth et al., 2012; Wang et al., 2020; Zhou et al., 2019). This is because a variety of factors controls the NO_x conversion efficiency and the NO_3^- content in PM, including precursor emission sources, complex multiphase chemical reactions with other reactive species, and environmental conditions (e.g., temperature, relative humidity, solar radiation) (Zhang et al., 2015). It remain difficult to assess the contribution of each parameter to the non-linear N_r chemistry, which is partly driven by close links between changes in aerosol acidity, gas-particle partitioning, and atmospheric oxidation capacity (Shah et al., 2018; Li et al., 2021b; Fu et al., 2020; Shi et al., 2019). Ozone (O_3) and hydroxyl radicals (OH) (Finlayson-Pitts and Pitts, 2000), are the major oxidants in the atmosphere whose chemical cycles are largely controlled by solar radiation. As a result, there are significant diurnal and seasonal variations in NO_x chemistry (e.g., Prabhakar et al., 2017; Alexander et al., 2020). Notably, NO_3^- formation is generally dominated by homogeneous OH oxidation and heterogeneous O_3 chemistry during day/summer and night/winter, respectively (Alexander et al., 2020). However, assessing the relative contributions of individual formation channels, together with their sensitivity to environmental parameters, is not straightforward and requires extensive in situ observations combined with modelling tools (e.g., Alexander et al., 2020; Brown, 2006; Newsome and Evans, 2017; Xue, 2022; Prabhakar et al., 2017).

Upon release into the atmosphere, NO_x, mainly emitted as NO, undergoes oxidation to form NO_2. During the day, a rapid photochemical equilibrium is established between NO and NO_2, known as the "photostationary state" (PSS; Leighton, 1961), via key interconversion reactions (Reactions R1−R3):

$$NO_2 + h\nu \xrightarrow{M} O(^3P) + NO \qquad\qquad \text{R1}$$
$$O(^3P) + O_2 \xrightarrow{M} O_3 \text{ with } M = N_2 \text{ or } O_2 \qquad\qquad \text{R2}$$
$$NO + O_3 \rightarrow NO_2 + O_2 \qquad\qquad \text{R3}$$

This cycle can be disturbed by peroxy radicals ($RO_2 \equiv$ hydroperoxyl radical (HO_2) + methyl peroxy radical (CH_3O_2)) via typically Reaction (R4):

$$NO + RO_2 \rightarrow NO_2 + RO \qquad\qquad \text{R4}$$

Note that in polluted atmospheres where NO_x mixing ratios often exceed ppb levels, Reaction (R4) followed by Reactions (R1)−(R2) lead to the formation of O_3 (Crutzen, 1979). Although the role of RO_2 in NO_x oxidation is crucial in O_3 formation and NO_x oxidation rate, measuring RO_2 mixing ratio remains challenging due to the need for state-of-the art instrumentation coupled with photochemical models to establish chemical budgets (e.g., Ren et al., 2006; Tan et al., 2018). While NO is usually oxidised relatively quickly into NO_2 in summer due to the high levels of O_3 and solar radiation, the shorter day length and lower temperature in winter result in a contrasted NO_x

cycling. In particular, the formation of a temperature inversion at the surface can trap pollutants emitted close to the surface in a shallow layer for hours to days (e.g., Largeron and Staquet, 2016; Olofson et al., 2009). Under those conditions, it is not uncommon for O_3 levels to be very low due to quasi-complete titration by NO, which can have further impacts on the atmospheric oxidation capacity. However, pronounced O_3 pollution episodes may also arise in winter in highly polluted areas, such as in oil-producing regions due to intense VOCs emissions (Edwards et al., 2014) or in China, where pollution control strategies mainly target NO_x while VOCs emissions remain more or less constant (Ren et al., 2022). In urban areas, NO_2 is generally mainly removed from the atmosphere by reaction with OH during the day via Reaction (R5) (Dentener and Crutzen, 1993):

$$NO_2 + OH \xrightarrow{M} HNO_3(g) \hspace{3cm} \text{R5}$$

NO_2 can also react with O_3 to form nitrate radicals (NO_3) via Reaction (R6):

$$NO_2 + O_3 \xrightarrow{M} NO_3 + O_2 \hspace{3cm} \text{R6}$$
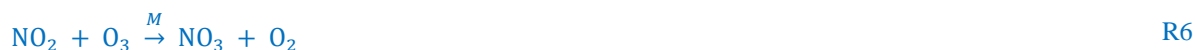
However, NO_3 is rapidly photolyzed during the day regenerating back NO_2 (Wayne et al., 1991). Another important NO_3 loss reaction is that with NO in polluted environments (Brown and Stutz, 2012). At night, without photolytic activity and lower precursor emissions, the lifetime of NO_3 radicals substantially increases. NO_3 reacts with NO_2 to form dinitrogen pentoxide (N_2O_5; Reaction R7), which then undergoes heterogeneous hydrolysis to form HNO_3 (Reaction R8):

$$NO_3 + NO_2 \xleftrightarrow{M} N_2O_5 \hspace{3cm} \text{R7}$$
$$N_2O_5 + H_2O(aerosol) \rightarrow 2\,HNO_3(aq) \hspace{2cm} \text{R8}$$

Reaction (R7) is temperature dependent, so N_2O_5 can eventually decompose to reform NO_2 and NO_3, with the N_2O_5/NO_3 ratio being negatively correlated with temperature. N_2O_5 is an important nocturnal sink for NO_x, notably in winter in urban atmospheres due to high aerosol loads and low temperatures. However, the efficiency of Reaction (R8) is difficult to determine because it strongly depends on parameters such as the aerosol surface density and its chemical composition (Brown, 2006), which are not often well characterised. In addition, NO_3 can react with hydrocarbons to produce HNO_3, which could significantly contribute to the formation of NO_3^- in industrialised regions with high hydrocarbon emissions (Brown et al., 2011). It is estimated that the Reactions (R1) to (R8) lead to the formation of 82 % of NO_3^- near the surface on a global scale (Alexander et al., 2020). In polluted environments, the respective contributions of Reaction (R5) (OH pathway) and Reactions (R6)−(R8) (N_2O_5 pathway) are more contrasted and are still debated (e.g., Chan et al., 2021; Fu et al., 2020). In addition, the reaction of N_2O_5 with chlorine on aerosols can contribute to NO_3^- production in urban atmospheres (Thornton et al., 2010), with further impacts on O_3 production in continental polluted atmosphere in winter (Wang et al., 2019a). Other reactions, such as those involving halogen and organic intermediates, may become significant for NO_3^- production in specific regions, such as in polar, oceanic, and coastal areas (Alexander et al., 2020; Penkett et al., 2007; Savarino et al., 2013; Simpson et al., 2015).

To help better constrain the atmospheric N_r chemistry and budget, the last three decades have seen a growing interest in stable oxygen (O) and nitrogen (N) isotopes, notably in NO_3^- (Elliott et al., 2019; Savard et al., 2018). The isotopic composition is reported as an isotopic enrichment (δ) with respect to a reference material, defined as $\delta = (R_{sample}/R_{reference} - 1)$, and expressed in per mill (‰). R refers to the elemental abundance ratio of the heavy isotope to the light isotope (e.g., $^{18}O/^{16}O$; $^{17}O/^{16}O$; $^{15}N/^{14}N$) in the sample, and in an international isotopic reference material (Vienna Standard Mean Ocean Water for O; Li et al., 1988, and atmospheric N_2 for N; Mariotti, 1984). A powerful tool to help trace the relative importance of different NO_x to NO_3^- oxidation pathways is through the use of the ^{17}O-excess ($\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$). $\Delta^{17}O$ is transferred to NO_3^- by O_3 which possesses a very unique $\Delta^{17}O$ ((26.2 ± 1.3) ‰; Vicars and Savarino, 2014) due to mass-independent fractionation during its formation process (Thiemens, 2006). In comparison, the $\Delta^{17}O$ of other atmospheric oxidants such as OH is near zero due to isotopic exchange with atmospheric water vapor (Dubey et al., 1997). Similarly, as the isotopic anomaly of atmospheric O_2 is very close to 0 ‰ (Barkan and Luz, 2003), and since RO_2 are mostly produced by the reactions $R + O_2$ and $H + O_2$, $\Delta^{17}O$ of RO_2 can be considered negligible (Alexander et al., 2020). Therefore, $\Delta^{17}O$ in NO_3^- represents a unique tracer of the O_3 implication in its formation processes, that can provide valuable constraints on the relative contributions of individual reactions (e.g., Morin et al. 2011, Alexander et al., 2009; Michalski et al., 2003). By a simple mass balance calculation of O atoms in NO_3^-, the ^{17}O-excess of NO_3^- produced by an individual NO_2 to NO_3^- conversion process i (($\Delta^{17}O(NO_3^-)_i$)) can be expressed as:

$$\Delta^{17}O(NO_3^-)_i = \frac{2}{3} \times \Delta^{17}O(NO_2) + \frac{1}{3} \times \Delta^{17}O(add. O)_i \qquad (1)$$

where $\Delta^{17}O(NO_2)$ is the ^{17}O-excess of atmospheric NO_2 and $\Delta^{17}O(add. O)_i$ is the transferrable ^{17}O-excess of the oxidant responsible for the conversion of NO_2 in NO_3^- (Michalski et al., 2003). From Eq. (1), if $\Delta^{17}O(NO_2)$ is constrained, one can derive individual $\Delta^{17}O$ transfer to NO_3^- relative to a i conversion process and compare this value with observed $\Delta^{17}O(NO_3^-)$.

Recent studies in urban areas have attempted to interpret the variability of $\Delta^{17}O(NO_3^-)$ in aerosols in order to quantify the relative contribution of homogeneous and heterogeneous processes to NO_3^- formation (e.g., Fan et al., 2023, 2022; He et al., 2020, 2018; Li et al., 2022b; Lim et al., 2022; Wang et al., 2023, 2019; Kim et al., 2023; Zhang et al., 2022b). However, to that end, it is necessary to have a clear quantitative understanding of the transfers of $\Delta^{17}O$ in the N_r cycle. To date, due to very limited observational data, there is a lack of well-establish knowledge on the dynamics of $\Delta^{17}O$ in NO_2, the key intermediate species in the formation of NO_3^-. Consequently, strong assumptions about $\Delta^{17}O(NO_2)$ have to be made when interpreting $\Delta^{17}O(NO_3^-)$ measurements, which could potentially lead to biased conclusions. Notably, the most difficult regions for the interpretation of NO_3^- records are potentially polluted areas where the isotopic composition of NO_2 is expected to be highly variable in space and time. Most studies typically estimate $\Delta^{17}O(NO_2)$ during the day by assuming that an isotopic steady state (ISS) is reached between NO_x and O_3 resulting in $\Delta^{17}O(NO_2)$ depending only on the relative contributions of different oxidants to NO oxidation. A recent study reported the first in situ observations of $\Delta^{17}O(NO_2)$ in an urban environment (Grenoble, France) in spring (Albertin et al., 2021). Time resolved NO_2 sampling (ca. 3 h) during 24 h revealed a strong diurnal cycle in $\Delta^{17}O(NO_2)$, reaching ca. 40 ‰ during the day and decreasing down to ca. 20

‰ at night. The observed $\Delta^{17}O(NO_2)$ values and dial variability were consistent with its expected behaviour derived from $\Delta^{17}O$ mass balance equations under the ISS assumption during the day. However, this first $\Delta^{17}O(NO_2)$ dataset is very short. More measurements are needed to test in different environments and season the applicability of this new isotopic tool and to assess whether the ISS is still valid. At night, the low $\Delta^{17}O(NO_2)$ measured by Albertin et al. (2021) is consistent with the oxidation of freshly emitted NO by O_3. Nonetheless, since the timescale for the oxidation of NO_2 into NO_3^- is thought to exceed the duration of the night (Alexander et al., 2020), it is also common to assume that the isotopic composition of nocturnal NO_2 reflects more daytime formation and conditions of the previous days. While this assumption may hold true in remote areas (Morin et al., 2011), significant uncertainties subsist in urban areas where the nighttime NO_3^- chemistry may be more efficient. In such circumstances, the production of NO_3^- from NO_2 formed at night would lead to a lower than expected $\Delta^{17}O$ transfer to NO_3^-. For these reasons, the dual survey of the O isotopic composition of NO_2 and NO_3^- would certainly help to accurately interpret $\Delta^{17}O(NO_3^-)$ observations in polluted atmospheres, particularly with sampling at sub-daily time scales which would allow to study the diurnal dynamics of $\Delta^{17}O(NO_2)$ and its links with $\Delta^{17}O(NO_3^-)$.

In addition to $\Delta^{17}O$, $\delta^{15}N$ in NO_3^- ($\delta^{15}N(NO_3^-)$) can be used as a tracer of NO_3^- sources and/or chemical processing. As different NO_x emission sources have often distinct $\delta^{15}N$-fingerprints depending on the NO_x production mechanism (Heaton, 1990; Felix et al., 2012; Fibiger and Hastings, 2016; Walters et al., 2015a, b; Yu and Elliott, 2017; Miller et al., 2018), $\delta^{15}N(NO_3^-)$ is a potentially valuable tool to trace the origins of its gaseous precursor. However, due to N fractionation effects associated with physico-chemical processing, $\delta^{15}N$ is altered during the conversion of NO_x to NO_3^- (Elliott et al., 2019). Therefore, the variability of $\delta^{15}N(NO_3^-)$ can be attributed to: (1) a change in NO_x emission sources and (2) N isotopic fractionations between NO and NO_2, between NO_2 and NO_3^-, and during the transport of NO_3^-. These effects co-exist with relative contributions varying according to environmental conditions and the mix of NO_x emissions. Numerous observations in diverse environments have emphasised the substantial influence of N fractionation effects in altering the original ^{15}N composition of emitted gaseous NO_3^- precursors (e.g., Bekker et al., 2023; Chang et al., 2018; Geng et al., 2014; Li et al., 2021; Luo et al., 2023; Vicars et al., 2013). Although some N fractionation factors are available from calculations (Walters and Michalski, 2015) and laboratory experiments (Li et al., 2020; Walters et al., 2016), there is still a lack of observational constraints on the magnitude of the N isotopic partitioning between NO_x and NO_3^-, which could lead to biased interpretations of $\delta^{15}N(NO_3^-)$ observations.

Following the preliminary work of Albertin et al. (2021), this study presents for the first time the simultaneous measurements of the atmospheric NO_2 and NO_3^- multi-isotopic compositions. The sampling took place at high temporal resolution (~ 3 h) in late February 2021 in an urban Alpine city. $\Delta^{17}O/\delta^{15}N$ data of NO_2 and NO_3^-, meteorological parameters, and atmospheric observations (NO, NO_2, O_3, and PM) are collated in order to investigate diurnal N_r chemistry, N fractionation effects and NO_x emissions. Our winter measurements extend the atmospheric NO_2 multi-isotopic composition record which is only composed of spring measurements performed during a single day by Albertin et al. (2021). The general aim of this case study is to test NO_2-based isotopic approaches for tracing the origins and fate of NO_x, for instance in urban areas on sub-daily time scales. The added value of $\Delta^{17}O(NO_2)$ measurements in N_r chemistry studies is more critically assessed here than in Albertin et al. (2021) through the use of accurate NO_x measurements. Besides, using the isotopic theoretical framework

developed previously, we explore the potential benefits of combining isotopic observations of NO_2 and NO_3^- to gain a more detailed and quantitative on the links between atmospheric N_r chemistry processes and variability in NO_2 and NO_3^- isotopic composition. The framework used in inferring dominant NO_x emission sources from NO_2 $\delta^{15}N$ measurements is also tested."

- **Line 60: be more specific quantitatively about what "the lowest temperatures" means**

The sentence has been rephrased in the revised manuscript as (lines 83-84):

"Reaction (R7) is temperature dependent, so N_2O_5 can eventually decompose to reform NO_2 and NO_3, with the N_2O_5/NO_3 ratio being negatively correlated with temperature."

- **Line 75: "…NO$_3^-$ is usually investigated in light of its ^{17}O-excess" – there are many studies that utilize $\delta^{18}O$ AND $\delta^{17}O$ because there are uniquely enriched in ozone, in addition to a focus on $\Delta^{17}O$. It is important to also incorporate the two studies mentioned above, one of which includes $\Delta^{17}O$ and $\delta^{18}O$ observations in both urban and suburban areas of the US. Please rephrase this line.**

We agree that the use of $\delta^{18}O$ in complement to $\delta^{17}O$ can be very valuable. However, as we do not use $\delta^{18}O$ in the manuscript, we prefer not to mention $\delta^{18}O$ for clarity and to avoid confusing the reader. However, we have added the measurement data of $\delta^{18}O$ in the revised Supplement as they are used to calculate $\Delta^{17}O$.

We have added the study by Kim et al. (2023) in the revised manuscript.

- **Line 87-88: The mention of ice cores and the lack of definition of AOC here is strange. This is not connected at all to the current study or the conclusions that can be drawn from the 2 days of measurements in France. Suggest removing this line and any discussion of ice core related data/conclusions.**

We agree and the line has been removed in the revised manuscript.

- **Line 95-104: This section should include an overview of the work of Albertin et al, 2021. The fact that lower values were found at night challenges previous understanding based on Morin et al (2011). This is not discussed in the current work, but should be presented here or summarized based on what appears in Albertin et al, 2021 to better set up the expectations for diurnal variability in the urban sampling site.**

The introduction has been modified/reworded in the revised manuscript accordingly (see the revised introduction in our response above).

With regard to the of Morin et al. (2011) study, we would like to stress that our results do not "challenge" Morin's model. They are perfectly in line with the transfer model. Simply, Morin's model inputs did not include any fresh NO_x resupply in the box model.

- **Line 109-110: This line does not include the fact that nitrate is also highly susceptible to large fractionations between the gas and particle phases. Why is that not included here and never discussion in the discussion? (see General comment and citations above)**

We do not discuss the N fractionation associated to the speciation of NO_3^- between the gas and particle phase because our sampling method is design to collect both HNO_3 and p-NO_3^- (see our response to your comment above) and it is the total nitrate that is the right metric to compare with NO_2. HNO_3 and p-NO_3^- are in permanent exchange between these two phases, (e.g., $H_2SO_4 + p$-$NO_3^- \rightarrow p$-$HSO_4^- + HNO_3$ is a well-known acid displacement reaction) and it is even possible that ^{15}N exchange happens which will add even more complexity. We do not believe that speciation is an added value for our transfer study. The mechanistical and methodological complexity is not worth it. This is why we deliberately ignore this discussion in the paper, as it will only add unnecessary and useless complexity.

Please note that we acknowledge that the significant change in $\delta^{15}(NO_3^-)$ during SP 2 in the presence of Saharan dust could reflect N fractionations related to a change of NO_3^- origin. This could be due to several reasons such as a change in NO_x precursors and/or in the contribution of NO_3^- formation pathways, especially if part of NO_3^- has a non-local origin. Our limited dataset (only two days) precludes drawing general conclusions but, rather highlights the sensitivity of our approach in investigating the sources and formation pathways of NO_3^- in complex environments.

- **The "during transport of NO_3^- in the atmosphere" should be a #3 here as it represents different process/processes than the prior 2 examples.**

We kind of agree. The idea here was to emphasise that the $\delta^{15}N$ of NO_3^- is determined by two main factors, namely the $\delta^{15}N$-fingerpring of the overall NO_x emission sources and the N fractionation effects that can alter the original $\delta^{15}N(NO_x)$ value. However, for the sake of comprehensiveness, we prefer to maintain the mention of the N fractionation effect associated with NO_3^- transport along with the other processes inducing N fractionation.

- **Line 113: remove or rephrase "which seemingly ignore the potential impact of post-emission fractionation" or find better references. The Hastings et al 2009 paper does not seem relevant here (it is based on ice core reconstruction – not at all comparable measurements to those taken here). Altieri et al. 2022 does not simply ignore this.**

We acknowledge that Hastings et al. (2009) is not directly relevant to the focus of our research, so it has been removed in the revised manuscript. Similarly, although we feel it is important to emphasise that N fractionation effects cannot be ignored in urban atmospheres, we agree to remove the citation of Altieri et al. (2022) in the revised manuscript. Nonetheless, Altieri et al. (2022) do ignore N fractionation effects (mentioned only once and the reason why they are not estimated is unclear/poorly explained) and the authors use their measured $\delta^{15}N$ of atmospheric nitrate directly to performed NO_x emission source apportionment. This approach is fundamentally flawed in regions affected by polluted air masses, as it is well addressed by Bekker et al. (2023).

Methods:

- **Line 141: Given that the area was partly covered in snow, and Savarino's rich literature on the impact of photolysis on snow nitrate and the release of NO_x from this source, with very depleted isotopic ratios. Why is this snow-sourced NO_x not included in the discussion here?**

In winter in Chamonix, the snow-sourced NO_x will likely be very small due to the short day length, the reduced irradiation time of the snow surface due to high altitude mountains surrounding the sampling site, and a large solar zenith angle. Additionally, it is very likely that the local flux of anthropogenic NO_x emissions far exceeds the potential flux from the snowpack. For these reasons, snow-sourced NO_x is not included in the discussion. Furthermore, as already mentioned above, data presented in Section 3.4.1 clearly show that N isotopic equilibrium effects between NO and NO_2 drive the main variability of $\delta^{15}N$ at our site and that there is one dominant source of NO_x at our site from road traffic.

- **Lines 141-145: Evidence must be provided to support the assumption that total nitrate is collected (HNO_3 gas and particulate nitrate). The studies cited do not prove this. This is an assumption made, and under the conditions in those studies, the alkaline quality of the aerosols was suggested to scavenge the HNO_3 onto the filters. Is this true in the case study here?**

Please refer to our response to your general comment #2.

- **It should be made clear here also what is being collected – i.e. total suspended particles or PM$_{10}$ or ?**

"TSP" means "total suspended particles". The full term has been added in the revised manuscript for clarity as (lines 183-184):

"Atmospheric particles (aerosols) were collected using a high-volume sampler (Digitel®, DH77, total suspended particle inlet, 1 m^3 min^{-1})"

- **For the preservation of samples prior to isotopic analysis, how is it ensured that there is not exchange between the nitrite analyte (for NO$_2$) and water? This has been shown to be extremely important and would yield incorrect results since the samples would no longer be representative of the atmosphere (see General comment and citations above)**

Please refer to our response to your general comment #2.

- **Line 155: This first sentence is difficult to understand. What does "corrected by the arithmetic mean" mean? Was it subtracted from all results? It is stated that is represents 8% ± 8% of what? The average total nitrate collected? Or is this the average of the average based on comparison of the blank concentration to each sample's concentration? It would be better to state the average concentration of the blanks here, perhaps compared against the overall average nitrate concentration, and more clearly state how this was "corrected" for to make this explicitly clear.**

We agree that the overall meaning of this sentence was not clear. In the revised manuscript, we have added information on filter blanks as (line 193):

"Two field blanks were performed to evaluate the initial content of trace elements and possible contamination during handling."

and rephrased line 155 as (lines 211-214 in the revised manuscript):

"Reported to the total filter surface, the NO$_3^-$ contribution from blank filters represented on average (8 ± 9) % of sampled NO$_3^-$. Atmospheric mass concentrations (expressed in µg m^{-3}) were calculated as the ratio of the total ion filter loading (corrected for the blank contribution) to the total volume of air pumped through the filter at STP conditions."

- **How many field blanks were collected? How were they collected? The impact of a high blank on one collection period is discussed several times later in the manuscript so clarity is needed here.**

We suppose you refer here to denuder sampling. This info has been added to the revised manuscript as (lines 229-236):

"The isotopic composition of NO_3^- samples was analysed in triplicate (the mean value of replicate measurements and the associated repeatability are reported in Table S2 in the Supplement). The limited amount of NO_2 samples did not allow for replicate measurements. From UV-vis analysis, all NO_2 samples presented a negligible blank ($<$ 4 %; mean of 1.7 nmol ml^{-1}) except for the sample collected between 13:30 and 16:30 LT during SP 2 which shown a blank around (14.0 $\pm$ 1.4) %. Therefore, the measured $\Delta^{17}O$ of this sample was corrected for blank effect assuming that the contaminated NO_2^- possessed a $\Delta^{17}O = 0$ ‰. No correction from this blank effect was applied on the $\delta^{15}N$ measurements of NO_2 because the $\delta^{15}N$ fingerprint of the contamination could not be characterised. This uncertainty is propagated in the calculations of section **Erreur ! Source du renvoi introuvable.** and considered in the discussions."

- **Line 177: Table S4 should be Table S3.**

Thanks for pointing out this error, this has been corrected in the revised manuscript.

- **What are the average measurement uncertainties based upon? Repeated measures of reference materials? And how many times were run?**

For each IRMS analysis set, the average measurement uncertainties is estimated based on the standard deviation of the residuals from the linear regression between the measured value of the reference materials and their expected values.

For the NO_3^- samples, as they were analysed in triplicate, i.e. analysed by three independent IRMS runs, we present here the average analytical error calculated on these three IRMS runs. For each IRMS analysis set, NO_3^- reference materials (n = 4) were prepared in different concentrations (n = 5), from 40 nmol to 140 nmol.

As the azide method is specific to NO_2^- ions, possible NO_3^- contamination of denuder extractions does not impact the isotopic analysis of collected atmospheric NO_2.

- **Additionally, it should be made clear here in the methods whether both nitrate and nitrite reference materials are necessary to be included in the separate runs for NO2 (as nitrite) and NO3- (as nitrate).**

This section has been for better clarity in the revised manuscript as (lines 236-243):

"Possible isotopic changes resulting from the conversion and analysis process of NO_3^- and NO_2 samples were evaluated using international NO_3^- and NO_2^- isotopic reference materials, respectively (Table S3 in the Supplement). Accuracy of the analytical method was estimated as the standard deviation (σ) of the residuals between measurements of the reference materials and their expected values. In our study, average measurement uncertainties on $\delta^{15}N$, $\delta^{17}O$, $\delta^{18}O$, and $\Delta^{17}O$ were estimated to be ±0.3 ‰, ±0.9 ‰, ±1.3 ‰, and ±0.4 ‰, respectively, for NO_3^- samples and ±0.3 ‰, ±0.4 ‰, ±0.9 ‰, and ±0.3 ‰, respectively, for NO_2 samples. Detailed information about the calibration procedure can be found in Morin et al. (2009) and in Albertin et al. (2021) for NO_3^- and NO_2 samples, respectively."

- **Line 183-184: Please clarify the "blank" here. Is this the field blank? Above it is stated that the blanks represented 8+/-9% so how is the mean here now 4%? Or is the previous blank about nitrate instead of nitrite? Were nitrate blanks also tested and what were the results?**

The (8 ± 9) % field blank is relative to NO_3^- samples, not NO_2. We have rearranged and reworded Section 2.2 in the revised manuscript for more clarity (see our response above).

- **Section 2.4.1: Please make it clear that $\Delta^{17}O$ is only conserved in processes that are fractionating…i.e., this would not be true if exchange were to occur.**

This has been specified in the revised manuscript as (lines 261-264):

"Because NO_2 and NO_3^- loss processes do not fractionate in terms of the oxygen mass-independent anomaly and considering that each source reaction induces a transfer of $\Delta^{17}O$ to NO_2 and NO_3^-, one consider the mass conservation of $\Delta^{17}O$ during fractionation processes in the N_r cycle. Hence, one can implement $\Delta^{17}O$ in the general mass balance equation of NO_2 and NO_3^-."

- **Line 224: What is the lifetime for NO_2 during the day against loss? Why is this not also calculated? The table states that the lifetime against photolysis is 5 min, what is the lifetime against conversion to nitrate? The case for daytime comparison with a three-hour difference (i.e. NO_2 now, compared to NO_3^- that was collected three hours later) needs to**

be better justified. If the NO₂ lifetime is only minutes (Table B1) than the time frames should be the same for comparing NO₂ and NO₃⁻.

This is very important. The lifetimes calculated are based on chemistry alone and do not seem to include wind speed or direction. For nighttime, it is stated that NO₂ has a 10 hour lifetime against loss (via deposition or chemistry). Therefore, the authors compare a single average nighttime measurement of NO₂ to NO₃⁻. In a closed system this would absolutely make sense. But in an open system, how can we ensure that the NO₂ collected during that time represents THE NO₂ that was converted to the sampled NO₃⁻? The authors make the assumption that this is true, then prove it by saying they can calculate the NO₃⁻ based on the measured Δ^{17}O-NO₂ – this seems circular.

If we consider an OH mixing ratio at ca. 2×10^6 molec cm^{-3} (average upper limit observed in different polluted environments at mid latitudes in winter; e.g., Tan et al., 2018; Stone et al., 2012) and $k_{NO_2+OH} = 1.2 \times 10^{-11}$ cm^3 molec^{-1} s^{-1} (Atkinson et al., 2004), the lifetime for NO₂ during the day against chemical conversion into HNO₃ (i.e., OH oxidation) would be ca. 12 h. With regard to dry deposition, if we consider a NO₂ dry deposition velocity of 0.25 cm s^{-1} (Holland et al., 1999) and a mean boundary layer height if 500 m, the lifetime for NO₂ during the day against dry deposition would be at an upper limit of ca. 56 h. Hence, NO₂ lifetimes against chemical loss and dry deposition are negligible in comparison with NO₂ photolysis which is about few minutes. However, what does really matter to compare ^{17}O-excess is NO₃⁻ residence time, and please refer to our response to your general comment #4 on this topic. Note that we have removed line 224 in the revised manuscript and reworded/added information as (lines 290-298):

"Assuming a mean NO₃⁻ deposition velocity of 0.5 cm s^{-1} (mean value of the dry deposition velocities of HNO₃ and p-NO₃⁻; Zhang et al., 2009), and considering the maximum daytime and minimum nighttime boundary layer heights of 500 and 100 m above ground level, respectively (estimations based on measured vertical temperature profiles; Fig. S2 in the Supplement), the estimated residence time of NO₃⁻ against dry deposition can reach up to 28 hours during the day, and 6 hours at night (Table B1). Therefore, on sub-daily time scales, the ^{17}O-excess in NO₃⁻ during the day is more likely to reflect a combination of daytime and nighttime production processes than during the night. Note that, our estimated residence times for NO₃⁻ against dry deposition are upper limits as they represent the time required to reduce by a factor e the concentration of NO₃⁻ present at the top of the boundary layer; NO₃⁻ close to the surface would have a much shorter residence time."

As the city of Chamonix is at an altitude of 1035 m and is located in an Alpine valley of ca. 2 km wide on average, surrounded by high-elevation mountains (up to 4810 m), we can consider that at night the valley floor is isolated from upper layers due to a stable temperature inversion layer characterised in previous studies (e.g., Chazette et al., 2005). Hence, we can assume in a first approach that at night the surface layer behaves as a close system due to weak vertical mixing, until the inversion layer breaks

down in the following daytime hours. Secondly, our approach is not to assert that the NO_2 present at the surface is that which is converted to NO_3^- (which we also sample), but rather to make this assumption and test whether isotopic mass balances support it. If isotopic mass balances do not match the observations, this means that the sampled NO_3^- does not originate solely from local oxidation of surface NO_2, as it is the case during SP 2.

- **Section 2.4.2 – I suggest the authors consider moving up the discussion of the Freyer, 1971 study in discussing the framework for interpretation of the isotopes. This is the closest relevant study to the current work for nitrogen isotopes.**

  Why is the fractionation of $HNO_3(g)$ versus $NO_3^-(p)$ ignored in this section? It should clearly be stated why this is not included. While the collection of total NO_3^- could mask this fractionation, this would only be the case if all of the nitrate gas and particles are locally derived. In other words, if gaseous nitrate is taken up on particles (e.g., see lines 326-330) transported to the observation site and collected as a sample, it will reflect fractionation of $HNO_3(g)$ versus NO_3^- (p) that may have not occurred locally. How is this accounted for? This seems like it could be particularly important in the SP 2 case.

Following your comment, we have added discussion on this topic in Section 3.4.3 of the revised manuscript. However, we do not discuss gas-particle N fractionation effects in Section 2.4.2 as we consider that both $HNO_3(g)$ and p-NO_3^- are collected (see our reply above). For clarity, we prefer to introduce gas-particle N fractionation effects only when we underline changes in the ^{15}N distribution between SP 1 and SP 2 in Section 3.4.3.

- **Line 268: what is the "daytime NO_2 chemistry lifetime" used here?**

As NO_2 lifetime regarding OH oxidation is negligible in comparison to NO_2 photolysis (see our response above), here the daytime NO_2 chemistry lifetime refers to NO_2 lifetime against photolysis, which is translated in the expression we give of $A_{day}{}^*$.

- **Section 3.1 – This section is largely discussion, not just results. It is indeed important to characterize the general atmospheric observations but the section includes a lot of "likely" descriptions of how to explain the atmospheric observations, not simply a presentation of the results. The section title should be modified to Results and Discussion or the discussion points should be moved to the appropriate section.**

As recommended, we renamed Section 3 "Results and Discussion" and revised accordingly the titles of the sub-sections. Here is the plan of the revised manuscript:

- **Lines 305-310: As mentioned above, it would be useful to discuss ozone titration in the introduction with a more focused introduction around urban day and night NO_x chemistry. Most of the section 3.1 is really discussion of the results, not results. This should be amended. Is it a hypothesis that O_3 titration occurred at 16:00 LT or do you have evidence of this?**

As recommended we have modified/reworded the introduction, it is more specific to urban environments (see our response above) and have merged sections Results and Discussion in a single section (see the revised manuscript structure above).

O_3 titration at 16:00 LT is supported by atmospheric observations (Figure 1) showing that O_3 rapidly drops at that time following the rapid increase of NO_x concentration.

- **Line 318: "It turns out that a Saharan dust episode began on February 23 (Fig S3 in the Supplement." This is simply stated as fact. What is the evidence for this? In the Fig S3 a more impressive dust event occurs on Feb 7th and looks like a short term "event". The time**

noted on the 23rd does not have a clear start and end and looks more like a large background enhancement. No transport information is provided (e.g. back-trajectories or the like). So how is this event known to be of Saharan dust origin? It is stated that this should lead to increase in coarse materials and high concentrations of alumino-silicates and potassium and calcium -- were these measured on these samples and can be shown as verification?

Thank you for highlighting this point which was also pointed out by Reviewer #1. We have now provided complementary information and observation in the revised Supplement that back up the dust event idea. We invite you to read our response to comment #2 of Reviewer #1 on this subject.

- **Line 329: "…the origin of NO_3^- during SP 2 at our site remains unclear…" – why is this case when line 318 stated as fact that it was Saharan dust? All of this needs much clarification!**

The presence of Saharan dust during SP 2 does not necessarily mean that there were exogenic nitrate inputs at our sampling site (i.e., not formed in the Chamonix area). So yes, despite the fact that there is no doubt that we had Saharan dust deposits during SP 2, we cannot quantitatively identify the impact of the presence of this dust on the nature of the NO_3^- collected during SP 2. Indeed, Saharan dust can promote both the formation of NO_3^- by heterogeneous hydrolysis and the condensation of HNO_3 already present in the atmosphere. The only statement we can make is that the change of O and N isotopic distribution of NO_3^- between SP 1 and SP 2 could be linked to the presence of dust but we cannot state it as a fact.

- **Lines 352-365: Here it is stated that the conditions for Chamonix and Beijing are significantly different. But comparisons are made anyway. So this comes across as convenient. For seasonal considerations, this study is limited to only 2 days of wintertime observations. Suggest you include comparison with Kim et al., ACP, 2023 to suggest patterns of expected seasonal behaviour for mid-latitude conditions.**

We agree that the conditions in Chamonix and Beijing are different. However, this is the only previous study that has carried out high temporal resolution (ca. 3 h) NO_3^- sampling as we have done in Chamonix. It is the only point of comparison. We therefore believe that it is important to mention this study, although any comparison of NO_3^- isotopic records between the two sites must be done with great care (which we have done). We have modified/reworded this section in the revised manuscript, adding an additional comparison with another study that have collected NO_3^- on day/night basis as (lines 497-516):

"Over the two sampling periods, $\Delta^{17}O(NO_3^-)$ varies significantly (from 18.3 ‰ to 28.1 ‰), with a weighted mean of (22.5 ± 3.1) ‰. While $\Delta^{17}O(NO_2)$ values are relatively similar during the two sampling periods, $\Delta^{17}O(NO_3^-)$ values are systematically higher during SP 2 than during SP 1, except during the 7:30−10:00 LT interval. $\Delta^{17}O(NO_3^-)$ in Chamonix is in the same range of most previous observations in urban environments (9−44 ‰; e.g., Kim et al., 2023; Wang et al., 2023; Fan et al., 2023; Zhang et al., 2022b; Lim et al., 2022; Li et al., 2022b), but lower than most values measured during the cold season which are typically >25 ‰. Unlike $\Delta^{17}O(NO_2)$, daytime and nighttime $\Delta^{17}O(NO_3^-)$ values at our site are not significantly different (p-value > 0.05, n = 14). Similarly, from 12 h resolved sampling in winter Beijing, He et al. (2018) found no significant difference between daytime and nocturnal $\Delta^{17}O(NO_3^-)$ and suggest that each sample reflects NO_3^- produced during both the day and night. From high-time-resolved (3 h) aerosol sampling in winter Beijing, Zhang et al. (2022b) reported $\Delta^{17}O(NO_3^-)$ values between 23.4 ‰ to 39.3 ‰, with higher values observed at night $((31.0 \pm 2.6)$ ‰) than during the day $((29.3 \pm 3.0)$ ‰). This diurnal behaviour of $\Delta^{17}O(NO_3^-)$ was attributed to the changes in the branching ratio of nocturnal and photochemical reactions on NO_3^- formation. In Chamonix, the range of $\Delta^{17}O(NO_3^-)$ values are very different from Zhang et al. (2022) observations, with consistently lower values and a distinct diurnal tendency. However, in the cases of $\Delta^{17}O(NO_3^-)$ measurements at sub-daily temporal scale, the atmospheric lifetime of NO_x and NO_3^- is critical for comparing $\Delta^{17}O(NO_3^-)$ records from one site to another. Pollutant levels and atmospheric conditions between Chamonix and Beijing are very different, notably in winter when Asian urban areas can experience severe haze pollution episodes with NO_3^- mass concentration exceeding 70 µg m^{-3}, which is over 10 times higher than in Chamonix (Lim et al., 2022; He et al., 2018; Zhang et al., 2022b). In such conditions, PM can reach several hundreds of µg m^{-3} for several days, which can significantly impact atmospheric processes involved in the formation of secondary species. Aside from the intrusion of Saharan dust during SP 2, the pollutant level in Chamonix is indicative of a moderately polluted region, with significant diurnal variations"

It is difficult to compare our measurements with Kim et al. (2023). First, $\Delta^{17}O$ have been measured separately for HNO_3 and p-NO_3^- in Kim et al. (2023), whereas we collected both HNO_3 and p-NO_3^-. Second, Kim et al. (2023) performed weekly samplings whereas we only have 2 days measurements at high temporal resolution (ca. 3 h).

- **Line 372: The expectation that the $\delta^{15}N$ would be similar with Walters et al (2018) does not seem justified. Those measurements were made in a very different setting (ie not a valley surrounded by mountains) and during the summer. Comparing with Freyer et al would make a lot more sense. Commenting on the range and variability from different studies also makes sense, but a direct comparison with Walters does not seem appropriate unless it is justified.**

We do not expect $\delta^{15}N$ of NO_2 to be similar to that measured by Walters et al. (2018), nor to that measured by Albertin et al. (2021). This is because, as you mentioned, the environmental conditions of these two studies (spring and summer in urban locations) differ significantly from our study site. The point of comparing our work with these two studies is to highlight the marked change in behaviour of

$\delta^{15}N(NO_2)$ as a function of environmental conditions. This section has been reworded in the revised manuscript to clarify the message we want to convey. In addition, we have added to the revised manuscript the study of Freyer et al. (1993) which showed this seasonal change of N fractionation effects as (lines 615–631):

"Over the two sampling periods, $\delta^{15}N(NO_2)$ shows substantial diurnal variability (from −10.0 ‰ to 19.7 ‰, n = 16) with a weighted mean of (4.0 ± 9.1) ‰. In contrast, Albertin et al. (2021) reported a weak diurnal fluctuation of $\delta^{15}N(NO_2)$ in spring in Grenoble, in a narrow range from about −12 ‰ to −10 ‰. In summer in an urban/suburban location, Walters et al. (2018) also observed a wide range of $\delta^{15}N(NO_2)$ values, however, unlike our study, these are almost consistently negative (from −31.4 ‰ to 0.4 ‰) with an overall mean at (−11.4 ± 6.9) ‰. As shown in Eq.(8), fluctuations in $\delta^{15}N(NO_2)$ reflect changes in NO_x emission sources and/or N fractionation effects, these latter being weighted by $1 - f_{NO_2}$ i.e., the more NO_x is under the form of NO, the greater the N fractionation effects (see Section 2.4). Hence, in the previous works of Albertin et al. (2021) and Walters et al. (2018), due to high f_{NO_2} (> 0.7), isotope effects were small (<2.7 ‰) and $\delta^{15}N(NO_2)$ was mostly driven by changing contribution of NO_x emission sources. At our site, f_{NO_2} shows a wider range, from 0.3 to 1.0, suggesting significant N isotopic fractionation effects, with minimum and maximum contributions corresponding to the highest and lowest observed value of $\delta^{15}N(NO_2)$, respectively. This pronounced seasonal behaviour of N isotope fractionation effects within the NO_x cycle has previously been outlined in the seminal study of Freyer et al. (1993). Overall, compared with summer, lower f_{NO_2} during winter months due to lower O_3 concentrations and higher NO_x emissions favour EIE between NO and NO_2, which also has a higher fractionation factor due to the lower temperatures (see Appendix B). Besides, this seasonal fluctuation of f_{NO_2} can be expected to be observed on smaller time scales, typically on the diurnal scale in urban areas where NO is generally fully oxidised into NO_2 at night due to a lower NO_x emission rate resulting in higher f_{NO_2} at night than during the day, as observed at our sampling (Figure 2)."

- **Line 419: This is a bit hard to follow. Prior to Equation (4) RO_2 is defined as $RO_2 = HO_2 + CH_3O_2$. Equation 4 thus does not include reaction with HO_2 separately. But this line makes it appear as if RO_2 is being calculated from HO_2 alone. Please clarify.**

- **Line 421: The calculated RO_2 values are NOT consistent between cases A and B. This is even less true for SP 2 than SP 1. On average, and considering the variability one could argue they are not statistically significantly different, but at each time interval there are significant differences between case A and case B. This is noted in the following sentences, but this should be made clear from the start when you are discussing a mean versus a particular time period.**

- **Then again on line 438 it is stated the "closeness between RO_2 estimates using $\Delta^{17}O(NO_2)$ observations and those from empirical calculations…" – this is simply not true. The**

concentrations calculated for the different cases are very different so deriving conclusions based on their sameness is inappropriate. Further, the sensitivity of $\Delta^{17}O(NO_2)$ to the chemical dynamics is not surprising and here it is what is being both hypothesized/tested and concluded, which is circular.

With regard to your three comments above, concerns about this section were also raised by Reviewer #1, who suggested that the comparison with Case B should be removed because there is too much uncertainty about the calculated values and about the applicability of the empirical formula to our site. We agree with both comments and have removed the comparison with Case B in the revised manuscript which now only discusses RO_2 derived from isotopic measurements. Here the revised Section 3.2 treating this subject (lines 420–466):

"Over the course of SP 1 and SP 2, $\Delta^{17}O(NO_2)$ shows a large diurnal variability (from 19.6 ‰ to 40.8 ‰) with a weighted mean ± one standard deviation of (25.2 ± 7.1) ‰. $\Delta^{17}O(NO_2)$ values during the day (7:30−18:00 LT, (28.5 ± 7.3) ‰) are significantly higher (p-value = 0.002, n = 16) than during the night (18:00−7:30 LT, (20.8 ± 1.0) ‰). By day, $\Delta^{17}O(NO_2)$ follows a similar increasing trend during SP 1 and SP 2, reaching a respective maximum of 40.8 ‰ between 13:30−16:30 LT and 35.0 ‰ between 10h30−13h30 LT. For both sampling periods, after sunset, $\Delta^{17}O(NO_2)$ stabilises between 21:00 and 7:30 LT at ca. 20 ‰. Using the same sampling methodology in a mid-latitude urban area in spring, Albertin et al. (2021) reported very similar $\Delta^{17}O(NO_2)$ values over the course of one day (20.5−39.2 ‰), following a comparable diurnal pattern. As presented above (Section 2.4.1), according to the ISS (isotopic steady state) framework, the variability of $\Delta^{17}O(NO_2)$ reflects changes in the relative contributions of Reaction (R3) ($NO + O_3$) and Reaction (R4) ($NO + RO_2$) to the overall production of NO_2. At our site, $\Delta^{17}O(NO_2)$ drops rapidly during the 16:30−18:00 LT interval to 23.3 ‰ and 20.9 ‰ during SP 1 and SP 2, respectively. Since, the isotope recycling rate in the NO_x-O_3 system is driven at first order by J_{NO_2} (Michalski et al., 2014), due to low solar radiation between 16:30−18:00 LT at our site, such a rapid drop of $\Delta^{17}O(NO_2)$ suggests that sampled NO_2 might not be at ISS anymore when the NO_2 photolysis is very slow, notably at the end of the day in winter. Therefore, we only consider that ISS holds between 7:30 and 16:30 LT in order to avoid the questionable end-of-the day measurements in our ISS-based analysis. At night (i.e., no ISS), the observed drop of $\Delta^{17}O(NO_2)$ in the early evening reflects the rapid replacement of NO_2 formed during the day by NO_2 produced during the night via the conversion of freshly emitted NO, in line with Eq.(5). Then, high NO_2 throughout the night, along with relatively low O_3, supports observations of low $\Delta^{17}O(NO_2)$ at night (i.e., ≈ 20 ‰).

Using Eq. (3**Erreur ! Source du renvoi introuvable.**), we derive from $\Delta^{17}O(NO_2)$ observations the relative contribution of Reaction (R3) ($NO + O_3$) to Reaction (R4) ($NO + RO_2$) in the formation of NO_2 (T_{NO+O_3}):

$$T_{NO+O_3} = \frac{\Delta^{17}O_{day}(NO_2)}{\Delta^{17}O_{NO+O_3}(NO_2)} \tag{12}$$

Between 7:30 and 16:30 LT, T_{NO+O_3} varies from 0.55 to 1.00 (Table 1), with a mean of 0.88 and 0.75 for SP 1 and SP 2, respectively. The NO + O$_3$ pathway is dominant between 13:30 and 16:30 LT, corresponding to the time when O$_3$ is highest (Figure 1). In contrast, the maximum contribution for the NO + RO$_2$ pathway is observed between 7:30 and 10:30 LT, when NO levels are high and rising continuously. Interestingly, previous studies reported a high sensitivity of RO$_2$ to changes in NO$_x$, particularly at high NO$_x$ levels (Ren et al., 2006; Stone et al., 2012). Sources of RO$_2$ in wintertime are mainly driven by the production of OH radicals from HONO photolysis, alkene ozonolysis, and formaldehyde photolysis (Tan et al., 2018). During winter, HONO plays a crucial role in NO$_x$/O$_3$/RO$_2$ chemistry, particularly in the morning, as its photolysis can potentially accelerate daytime oxidation processes, leading to increased RO$_2$ production (Alicke et al., 2003; Aumont et al., 2003). Direct emissions from vehicle exhaust could be significant a source of VOCs and HONO at our site (Brulfert et al., 2005; Gu et al., 2019; Kirchstetter et al., 1996; Kurtenbach et al., 2001; Liu et al., 2023). Heterogeneous processes on ground surfaces and aerosols can also contribute to HONO formation (Aumont et al., 2003). In addition, snowpack releases may also be a potential source of HONO (Grannas et al., 2007), as detected in Paris after a snow event, which could significantly impact the urban OH budget (Michoud et al. 2015).

Following the approach of Albertin et al. (2021), combining Eqs. (3) and (4) allows to derive RO$_2$ mixing ratio from observed $\Delta^{17}O(NO_2)$ and O$_3$ mixing ratio following:

$$[RO_2] = \frac{k_{NO+O_3}[O_3]}{k_{NO+RO_2}}\left(\frac{\Delta^{17}O_{NO+O_3}(NO_2)}{\Delta^{17}O_{day}(NO_2)} - 1\right) \tag{13}$$

Between 7:30 and 16:30 LT, we estimate an average RO$_2$ mixing ratio at our site of (0.88 ± 0.88) pmol mol^{-1} and (4.92 ± 5.16) pmol mol^{-1} during SP 1 and SP 2, respectively (Table 1). Studies conducted in urban winter environments reported RO$_2$ measurements at a few pmol mol^{-1} (Ren et al., 2006; Emmerson et al., 2005; Tan et al., 2018; Kanaya et al., 2007), in good agreement with our estimations. Similarly, RO$_2$ mixing ratios derived by Albertin et al. (2021) from observed $\Delta^{17}O(NO_2)$ in spring (mean of (13.8 ± 11.2) pmol mol^{-1}) were also found to be in line with studies conducted in the same season. The fact that our isotopic inference of RO$_2$ mixing ratios carried out in two different seasons (winter and spring) are both comparable to direct in situ RO$_2$ measurements confirm the sensitivity of our method in probing the NO$_x$/O$_3$/RO$_2$ chemical dynamics. We think that our method may be very valuable in deciphering oxidation processes of N$_r$ species, down to sub-daily temporal scales. Nonetheless, we recognise that without concurrent in situ measurements of RO$_2$ and $\Delta^{17}O(NO_2)$, it is not possible to validate unambiguously the quantitative estimation of RO$_2$ levels with our method."

and the updated Table 1:

Sampling interval (start - end)	T_{NO+O_3}	RO_2 /pmol mol^{-1}
SP 1		
20/02 07:30 - 20/02 10:30	0.72 ± 0.01	0.86 ± 0.75
20/02 10:30 - 20/02 13:30	0.91 ± 0.01	1.77 ± 0.36
20/02 13:30 - 20/02 16:30	1.00 ± 0.01	0.00 ± 0.91
Mean	*0.88*	*0.88*
Std dev.	*0.14*	*0.88*
SP 2		
24/02 07:30 - 24/02 10:30	0.55 ± 0.01	0.58 ± 1.67
24/02 10:30 - 24/02 13:30	0.86 ± 0.01	3.56 ± 0.50
24/02 13:30 - 24/02 16:30	0.84 ± 0.08	10.63 ± 6.75
Mean	*0.75*	*4.92*
Std dev.	*0.18*	*5.16*

Table 1. T_{NO+O_3} and RO_2 mixing ratio (mean value $\pm$ overall uncertainty) derived from the isotopic measurements.

- **Line 471: the sentence beginning with "To note…" does not make sense. Please rephrase as I am unclear on the scientific meaning here. The contribution of blank versus sample should be better stated again. Not sure what "pondered by the mean" means.**

This section has been reworded/modified in the revised manuscript for more clarity as (lines 550-554):

"It is important to point out that, although the NO_2 sample collected on Feb 24 between 13:30 and 16:30 LT presents an important blank (ca. 14 %), ambient NO_2 is low during the sampling period (mean of (4.5 ± 1.8) nmol mol^{-1}). Therefore, as each $\Delta^{17}O$ value used to estimate $\Delta^{17}O_{calc}(NO_3^-)$ is weighted by the mean ambient NO_2 mixing ratio over the sampling period, the incertitude related to this blank has little influence on the daily average of $\Delta^{17}O_{calc}(NO_3^-)$."

- **Lines 476-478: I am interpreting here that the emphasis is on "processes" meaning the same expected chemistry for both nighttime sampling times. This seems overly simplified given that SP 2 was impacted by dust events and SP 1 was not. Is there no impact of dust on the nighttime chemistry? This should impact the reaction rates for N_2O_5. But also note that not all reactions are included in the case study here – for instance NO_2 hydrolysis, which could be impactful with heavier dust loading (see Alexander et al., 2020 for example). I think a bit more clarity is needed to separate the two case studies. If differences in conditions between the two sampling periods (i.e. gas and particle concentrations) are not being considered in the context of the chemistry then it challenges the conclusion that transported nitrate has to play a role in explaining the nighttime SP 2 data. (Note that I**

think the additional nitrate from aloft is a good explanation for the higher than expected $\Delta^{17}O$, but this needs to be set up better).

This section has been reworded/modified in the revised manuscript for more clarity as (lines 554-560):

"Given the low $\Delta^{17}(NO_3^-{}_{calc} - NO_3^-{}_{obs})$ during SP 1, observed $\Delta^{17}O(NO_3^-)$ can be explained by the local and rapid (< 12 h) oxidation of NO_2, dominated by the OH and N_2O_5 pathway during the day and night, respectively. However, in contrast to SP 1, the ^{17}O-excess measured in NO_3^- during the day of SP 2 cannot be fully constrained by the oxidation of surface NO_2 through the OH pathway, suggesting that the formation mechanisms of NO_3^- are different between SP 1 and SP 2 and/or the presence of NO_3^- not formed locally during SP 2. Below we examine the changes in the sub-daily dynamics of $\Delta^{17}O(NO_3^-)$ between SP 1 and SP 2 in light of atmospheric observations."

We had to analyse SP1 and SP2 with the same framework before finding a rather strong disagreement for SP2. We agree that it is very tempting to attribute the higher than expected $\Delta^{17}O$ for SP2 to additional nitrate originating from aloft but we cannot prove it. We also agree that Saharan dust can change/promote oxidation pathways to NO_3^-.

- **Line 515-516: Needs clarifying. The nitrate does not represent "deposition" so this phrasing needs to be changed here and through the rest of the manuscript. The samples represent aerosol (+gas) loaded onto a filter – so this does not represent deposition. Perhaps rephrase to "…during SP 2 may have increased the NO_3^- loading aloft, in comparison to SP 1."**

Thank you for pointing this out, the sentence has been reworded accordingly in the revised manuscript.

Section 4.3

- **The interpretation of the oxygen isotopic composition discussed the likely potential for photolysis of HONO to add significantly to the local oxidant budget. This is not mentioned at all as part of the nitrogen isotopic composition discussion, but this process would also produce NO with a very different $\delta^{15}N$. Furthermore, vehicle emissions could also be adding HONO, given that they are concluded as the primary source of local NO_x and NO_3^-. These pathways are neglected in the chemistry calculations and HONO impact on the $\delta^{15}N$ assumptions should be discussed or justified as to why be ignored.**

Please, see our response to your General comment #5. Besides, no measurement have been reported on the $\delta^{15}N$ of NO produced from HONO photolysis, therefore, we cannot state that it would be very different from dominant NO_x sources at our site.

- **Line 554-555: This result only holds for GP 2, i.e. only EIE regime. This sentence should be more specific.**

The section has been reworded in the revised manuscript for more clarity as (lines 660-667):

"The close match between the calculated average F_N of GP 2 and the observed F_N ((43.6 ± 3.3) ‰; slope of the regression line in **Erreur ! Source du renvoi introuvable.**) provides strong evidence for the reliability of Eq. **Erreur ! Source du renvoi introuvable.**), as well as the expression of $\alpha_{EIE(NO_2/NO)}$ used therein, to accurately describe the N fractionation between NO_x emissions and NO_2 at our site, and hence, to describe most of the variability of $\delta^{15}N(NO_2)$ measurements. This result holds significant importance in confirming the theoretical N isotopic fractionation framework used in prior research studies. It is also important to stress the influence of LCIE effects for GP 1, highlighting the high dependency of $\delta^{15}N(NO_2)$ to local environmental conditions. According to the A^* factor, a greater influence of LCIE in mid-afternoon could have contributed to the outlying of the two samples collected between 13:30 and 16:30 LT (GP 1)."

- **Line 588-589: In fact, Miller et al., (2017) in an on-road study showed no dependence on most of these factors (except heavy emitters, e.g. presence of diesel trucks). Heaton, 1990 only measured vehicles with none of the modern catalytic convertor technology. Felix and Elliott (2014) measurements were taken in a tunnel and are not representative of on-road traffic. Walters et al. represents tailpipe measurements. Miller et al. and Zong et al. represent on-road and near-road sites. Please use more consistent studies and/or justify the use of averaged values across studies that are not similar and/or not representative of the current environment being studied.**

Thank you for pointing this out, it is a common issue in our research community. We acknowledge that the selected value may not be the most accurate to represent our sampling site. Nonetheless, it is difficult to determine the most appropriate value given the specific characteristics of our sampling site. Chamonix is located in a deep valley encompassed by high altitude mountains. As a result, emissions of NO_x at the surface are confined, particularly in winter. Hence, it is likely that ambient NO_x at our site in the early morning are affected by fresh emissions trapped in the inversion layer. These conditions differ from the Miller et al. (2017) study carried out in a non-montainous region during spring/summer and along densely used roads. Temperature conditions and vehicle uses are very different in Chamonix. Second, our sampling site is situated in a residential area, and thus, we anticipate the influence of fresh and cold NO_x emissions in the morning when individuals leave their homes for work. Subsequently, during the day, we concur that NO_x emissions from vehicles are likely to be more influenced by two closely situated and major roads, namely Départementale 1506 and Nationale 205 which connect to the Mont-Blanc tunnel. Therefore, we can expect that the $\delta^{15}N(NO_x)$ becomes close to that of Miller et al. (2017).

For these reasons, we think it is more pertinent to refer to the Zong et al. (2017) value and then interpret the variability around this value in light of the specific conditions experienced during the day. As stated in the manuscript, our average $\delta^{15}N(NO_x)$ derived from corrected $\delta^{15}N(NO_2)$ is similar to that of Zong et al. (2017). Besides, we observe a slight increase of $\delta^{15}N(NO_x)$ during the day, with the highest value around midday. This is consistent with the study of Miller et al. (2017) and is likely influenced by background NO_x from traffic emissions of the two main roads situated a few hundred meters away. In contrast, the lower $\delta^{15}N(NO_x)$ observed in the early morning, when the inversion layer still exists, align with the study of Walters et al. (2015b) from tailpipe measurements.

In response to your concern regarding the studies selected by Zong et al. (2017) to derive their mean traffic $\delta^{15}N(NO_x)$ value, it is worth noting that a recent study by Song et al. (2022), adopted a similar method. However, Song et al. (2022) reviewed a greater number of studies, including Miller et al. (2017), in their calculations of the mean $\delta^{15}N(NO_x)$ for traffic. Song et al. (2022) obtained a very similar result to Zong et al. (2017) with a value of (-7.1 ± 4.1). Apologies for missing this study in the first version of the manuscript. Since Song et al. (2022) study takes into account more studies, we suggest to use their value as a reference for traffic $\delta^{15}N(NO_x)$. The revised manuscript includes this value as (lines 694-699):

"Regarding road traffic emissions, we have to stress that $\delta^{15}N$ values reported in the literature are rather variable mainly because N fractionations during the process of NO_x production can vary depending on the type of fuel used, the type of vehicle, the presence of an emission control system, and the time of commuting (Ammann et al., 1999; Felix and Elliott, 2014; Heaton, 1990; Miller et al., 2017; Walters et al., 2015b; Zong et al., 2020, 2017). We use here the mean vehicle-emitted $\delta^{15}N(NO_x)$ value given by Song et al. (2022) at (–7.1 ± 4.1) ‰, calculated from 181 measurements reported in the literature."

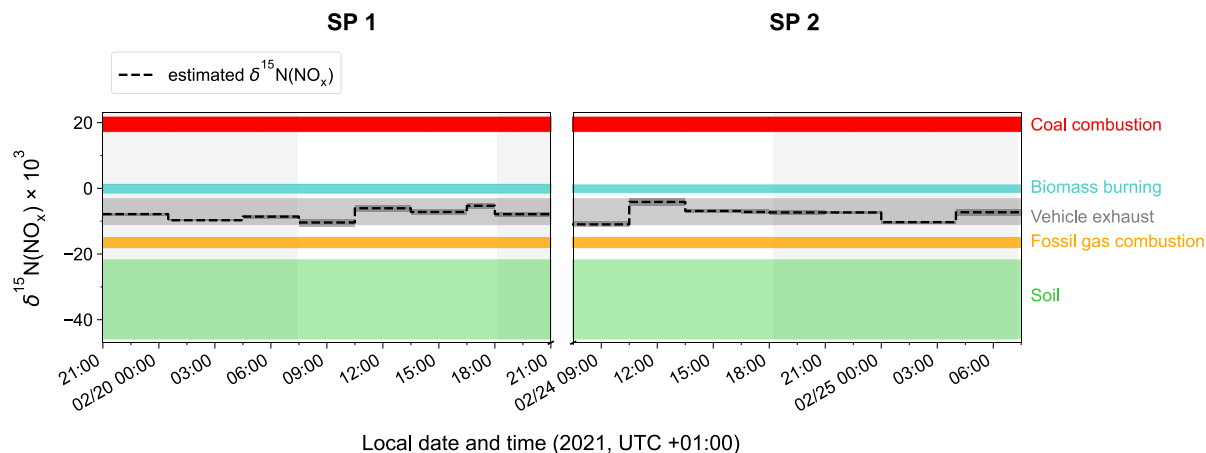and Figure 4 has been updated accordingly:

Figure 4. Time evolution of $\delta^{15}N(NO_x)$ (black dashed line) estimated from $\delta^{15}N(NO_2)$ observations in Chamonix after correction of N fractionation effects (length of horizontal line = sampling period, black shaded area = overall calculation error bar). Coloured shaded areas represent the standard deviation of the mean $\delta^{15}N$ value of individual NO_x emission source (coal combustion in red, biomass burning in blue, vehicle exhaust in grey, fossil gas in orange, and soil emissions in green). Grey backdrop shaded areas represent the nighttime (sunset to sunrise).

Note that it does not change the conclusion regarding the dominant NO_x source.

In your comment, you underline that cold starts are brief, yet they emit the most NO_x, which means that we ought to detect the highest levels of NO in the morning rather than in the late afternoon. This is confirmed by Figure 1 of the manuscript showing much higher NO mixing ratios in the morning. However, we also acknowledge that the large uncertainty on the heating oil $\delta^{15}N(NO_x)$ precludes a definite conclusion on our estimated $\delta^{15}N(NO_x)$ reflecting only traffic emissions. It is possible that heating oil emissions play a role. However, $\delta^{15}N(NO_x)$ of heating oil is not reported in the literature. The N content in distillate oil is negligible, similar to that of petrol, diesel, and fossil gas. This implies that the NO_x emission during its combustion can be classified as "Thermal-NO_x" (in contrast with "Fuel-NO_x"; Miller and Bowman, 1989). Thermal NO_x is generally depleted in ^{15}N owing to kinetic fractionation effects when the N_2 triple bond is broken, favouring the dissociation of the lightest isotopologue (Walters et al., 2015b). The mechanisms by which NO_x is produced by thermal processes vary according to combustion conditions such as temperature, pressure, and oxygen availability. These conditions affect the N fractionation extent. It is therefore challenging to predict precisely the $\delta^{15}N$ footprint of NO_x emitted from oil burner exhausts. It can be inferred that it would be near that of diesel vehicle exhausts and fossil gas burners i.e., approximatively somewhere between -17 ‰ and -13 ‰ (Walters et al., 2015a, b). Hence, the lower $\delta^{15}N(NO_x)$ values in the morning can also be due in part to heating oil emissions. These aspects are detailed in the manuscript.

- **Line 598-602: Some care needs to be taken here. It only takes about 30-50 seconds for an engine equipped with a catalytic convertor to be "warm" – in fact in the Walters' study Figure 2, the NO_x emission plateaus after ~50 seconds. It is challenging to believe that this is having such a large impact on early morning versus later daytime values given the 3-hour time period over which the $\delta^{15}N$ values are collected. Perhaps the authors could do a back of the envelope type calculation to confirm whether this suggestion is valid. Cold engines will emit very high concentrations of NO for a very short period, so could potentially impact NO_x loading – is there evidence of this in the gas phase measurements? i.e. given similar traffic conditions in the early morning and late in the day the concentrations should be much higher under "cold start" conditions.**

Please, see our response to your comment above.

- **Line 601: "removal" should be "replacement" (not sure how NO_x removes NO_x in this scenario?)**

Thank you for pointing this out, the word has been changed accordingly in the revised manuscript.

Summary and implications

- **Line 662: add "local" as in "…independently of the local NO_2 to NO_3^- conversion processes."**

Thank you for pointing this out, the word has been added accordingly in the revised manuscript.

- **Line 663: In the framework here, dry deposition takes NO_3^- out of the system so please rephrase. Do you mean that nitrate production is more likely or do you mean that the particle nitrate is heavy enough to sink and mix into the boundary layer?**

Thank you for pointing out this ambiguity, we actually want to refer to nitrate production through heterogeneous processes. The section has been modified/reworded in the revised manuscript as (lines 789-798):

"We use $\Delta^{17}O$ mass balance equations of NO_3^- constrained by observed $\Delta^{17}O(NO_2)$ to assess whether NO_3^- could originate locally from the oxidation of NO_2 at our site. During the first day of sampling, $\Delta^{17}O$ records of NO_2 and NO_3^- support the local oxidation of NO_2 to NO_3^- by OH radicals during the day, and via the heterogeneous hydrolysis of N_2O_5 during the night. The second day of sampling was affected by a Saharan dust event,

accompanied by notable changes in the isotopic composition of NO_3^-. We propose that the formation of a surface inversion layer at night could have influenced the vertical distribution of $\Delta^{17}O(NO_2)$ and resulted in a positive gradient of $\Delta^{17}O(NO_3^-)$ with altitude, independently of the local NO_2 to NO_3^- conversion processes near the surface. In such scenario, the presence of Saharan dust could have promoted heterogeneous NO_2 oxidation leading to higher $\Delta^{17}O$ in NO_3^- formed aloft. The latter would have then mixed with the NO_3^- formed near the surface when the inversion breaks up during the day. Although still uncertain, the influence of the boundary layer dynamics on the distribution of $\Delta^{17}O$ in NO_3^- should be investigated in the future, notably for urban areas in winter."

- **Line 682: perhaps add "…to test the hypotheses raised here." At the end of the line? It's not clear that there is evidence for a vertical gradient (yet) though the hypotheses raised in this work are certainly compelling.**

Thank you for this comment, the sentence has been reworded in the revised manuscript as (lines 818-820):

"In addition, the vertical distribution of NO_2 and NO_3^- isotopic composition should be documented in order to explore the possible role of the boundary layer dynamics in the variability of NO_2 and NO_3^- isotopic composition observed at the surface."

Technical comments:

- **Line 33: add () around NO and NO_2, i.e. (NO) … (NO_2) as they are being defined here**

Thank you for pointing this out, which has been corrected accordingly in the revised manuscript.

- **Line 49: the Leighton reference has a typo with the added "1961 citation"**

Thank you for pointing this out, which has been corrected in the revised manuscript.

- **Line 50: suggests adding in reaction #'s in text and () around HO_2 and CH_3O_2. For example, "This cycle can be disturbed by peroxy radicals (via R4; RO_2 = hydroperoxyl radical (HO_2) + methyl peroxy radical (CH_3O_2)) leading to formation of O_3 (via R2) (Crutzen, 1979)." Similarly R1-R3 should be called out in the text on lines 46-49.**

Thank you for pointing this out, which has been added accordingly in the revised manuscript.

- **Line 58: "Reaction R7" should be just "R7" (ie R implies the word "Reaction")**

We have followed the ACP notation which presents reaction numbers like this : Reaction (RX), Reactions (RX) to (RY), Reactions (RX)-(RY), and (Reaction RX). However, we have noticed a few typos in the manuscript which have been corrected according to this notation.

- **Line 101: "Authors" should be "The authors" or given the overlap in authors perhaps "We" ?**

Thank you for pointing out this error. Please note to that we have reworded and revised this paragraph in the revised manuscript (see our response above with the revised introduction).

- **Line 129: rephrase "The first study case" to This case study is the first to carry out concurrent multi-isotopic…."**

Thank you for pointing this out, please refer to our response above with the revised introduction.

- **Line 133: "conduction" should be "conducted"**

Thank you for pointing it out, which has been corrected in the revised manuscript.

- **Equation (6) and (7) should contain the subscripts day and night for NO_2 as well. i.e. make it clear that for the nighttime nitrate the NO_2 comes from Eq. 5.**

Thank you for pointing this out, which has been added accordingly in the revised manuscript.

> **Can you also clarify why equation 5 uses $\Delta^{17}O$-NO_2 at night rather than $\Delta^{17}O$-O_3? The only production channel at night is assumed to be $NO+O_3$, with presumably 1 oxygen from ozone and 1 from NO. Is it just implicit that $\Delta^{17}O$-NO_2 formed at night = $\Delta^{17}O$-O_3? This seems weird to not make this explicitly clear.**

Equation 5 uses $\Delta^{17}O_{night}(NO_2)$ and not $\Delta^{17}O(O_3)$ because it includes the residues of $\Delta^{17}O_{day}(NO_2)$. $\Delta^{17}O_{night}(NO_2)$ would be equal to $\Delta^{17}O(O_3)$ only when x, the fraction of NO_2 formed during the day to the total NO_2 measured at night, would be equal to 0.

- **Line 246: "later" should be "latter"**

Thank you for pointing this out, which has been corrected in the revised manuscript.

- **Line 246-247: This should be referenced to Li et al (2020) here. (it is not original to this work here)**

We recognise that this is not original to our work, but neither it is original to that of Li et al. (2020), although we agree the latter was the first to investigate in details the three isotopic effects in the NO_x cycle. KIE, EIE, an PHIFE result from the isotopic fractionation theory, therefore we have added as references in the revised manuscript the reviews that deal with these theoretical concepts, namely Miller and Yung (2000) and Young et al. (2002).

- **Line 250: "of the fraction of NO_x in the form of NO_2" is awkward phrasing, please rephrase.**

Thank you for pointing this out, which has been reworded in the revised manuscript as (lines 311-313):

"A general expression for $\delta^{15}N(NO_2)$ can be derived as a function of a factor F_N which represents the overall N isotopic fractionation effects between NO_x emissions and NO_2 (expressed in ‰), the fraction of NO_2 with respect to NO_x ($f_{NO_2} = [NO_2]/[NO_x]$), and of $\delta^{15}N(NO_x)$ (Albertin et al., 2021; Li et al., 2020)"

- **Line 286: "schematises" is not correct – rephrase.**

Thank you for pointing this out, the sentence has been reworded in the revised manuscript as (lines 347-349):

"The dominant NO_x to NO_3^- conversion processes considered in this study, along with corresponding $\Delta^{17}O$ transfer factors and the known ^{15}N enrichment factors at 298 K (determined from both experimental and computational studies) are illustrated in Figure C1."

- **Line 275: [NO_2] in the denominator should be [NO], correct?**

[NO_2] being at the denominator is correct as $(1/k_{NO+NO_2}[NO_2])$ is the NO lifetime with respect to isotopic exchange with NO_2.

- **Line 309: suggest rephrasing to "…recovers and stay relatively low throughout the night…"**

Thank you for pointing this out, which has been corrected accordingly in the revised manuscript.

- **Line 344-345: rephrase here – Δ^{17}O-NO$_2$ is ONLY similar for two of the time periods, not during the whole daytime. The observations at 13:30-16:30 at SP2 are questionable, and then the 16:30-18:00 samples are 3 per mil different. So overall, they are more different than similar for these time periods.**

This section has been modified/reworded in the revised manuscript as (lines 420-437):

"Over the course of SP 1 and SP 2, Δ^{17}O(NO$_2$) shows a large diurnal variability (from 19.6 ‰ to 40.8 ‰) with a weighted mean ± one standard deviation of (25.2 ± 7.1) ‰. Δ^{17}O(NO$_2$) values during the day (7:30−18:00 LT, (28.5 ± 7.3) ‰) are significantly higher (p-value = 0.002, n = 16) than during the night (18:00−7:30 LT, (20.8 ± 1.0) ‰). By day, Δ^{17}O(NO$_2$) follows a similar increasing trend during SP 1 and SP 2, reaching a respective maximum of 40.8 ‰ between 13:30−16:30 LT and 35.0 ‰ between 10h30−13h30 LT. For both sampling periods, after sunset, Δ^{17}O(NO$_2$) stabilises between 21:00 and 7:30 LT at ca. 20 ‰. Using the same sampling methodology in a mid-latitude urban area in spring, Albertin et al. (2021) reported very similar Δ^{17}O(NO$_2$) values over the course of one day (20.5−39.2 ‰), following a comparable diurnal pattern. As presented above (Section 2.4.1), according to the ISS (isotopic steady state) framework, the variability of Δ^{17}O(NO$_2$) reflects changes in the relative contributions of Reaction (R3) (NO + O$_3$) and Reaction (R4) (NO + RO$_2$) to the overall production of NO$_2$. At our site, Δ^{17}O(NO$_2$) drops rapidly during the 16:30−18:00 LT interval to 23.3 ‰ and 20.9 ‰ during SP 1 and SP 2, respectively. Since, the isotope recycling rate in the NO$_x$-O$_3$ system is driven at first order by J_{NO_2} (Michalski et al., 2014), due to low solar radiation between 16:30−18:00 LT at our site, such a rapid drop of Δ^{17}O(NO$_2$) suggests that sampled NO$_2$ might not be at ISS anymore when the NO$_2$ photolysis is very slow, notably at the end of the day in winter. Therefore, we only consider that ISS holds between 7:30 and 16:30 LT in order to avoid the questionable end-of-the day measurements in our ISS-based analysis. At night (i.e., no ISS), the observed drop of Δ^{17}O(NO$_2$) in the early evening reflects the rapid replacement of NO$_2$ formed during the day by NO$_2$ produced during the night via the conversion of freshly emitted NO, in line with Eq. (5). Then, high NO$_2$ throughout the night, along with relatively low O$_3$, supports observations of low Δ^{17}O(NO$_2$) at night (i.e., ≈20 ‰)."

- **Line 358: Is this Zhang et al, 2022a or 2022b?**

Thank you for pointing this out, this is Zhang et al. (2022b), it has been corrected in the revised manuscript.

- **Line 368: add "from" after "Aside" – i.e ."Aside from the intrusion…"**

Thank you for pointing this out, which has been corrected accordingly in the revised manuscript.

- **Line 385: "targeted" should be "found"**

Thank you for pointing this out, which has been corrected accordingly in the revised manuscript.

- **Line 392: Add "observed" in the figure caption to be sure reader follows that the $\Delta^{17}O$ values here are observed not calculated.**

Thank you for pointing this out, which has been added accordingly in the revised manuscript.

- **Line 412: this could use some rephrasing – it sounds here as if ozone were high over the whole time period. Perhaps rephrase to make clear that ozone peaks at 16:30 LT but is not high through the whole time from 10:30 – 16:30 LT.**

Thank you for pointing this out. For more clarity, we have shortened the described period to 13:30–16:30 LT, which corresponds to the highest observed O_3 mixing ratios. See the reworded Section 3.2 of the revised manuscript in our response above.

- **Line 420: The equations number in the text do not match those in the Table 1 footnotes.**

Thank you for pointing this out, which has been corrected in the revised manuscript.

- **Line 433: rephrase to "could be a significant source of VOCs…."**

Thank you for pointing this out, which has been rephrased in the revised manuscript.

- **Line 423: "…could be due to the important blank associated with this sample." The real issue here is the % contribution of the blank versus sample so perhaps rephrase to make that clear; currently it is not clear what "important blank" means.**

Thank you for pointing this out. This sentence has been removed because we have suppressed study case B. See the modified/reworded Section 3.2 of the revised manuscript in our response above.

- **Line 427: "The highest contribution of RO_2…is correlated with the highest NO levels."
  For this to be stated it must be shown to be true. The highest NO levels occur around
  10:30-11am at both SP1 and SP2. This is not the time of the highest RO_2 concentrations.
  This IS the time of the lowest T_{NO+O_3} which means that the relative contribution of RO_2 is
  high, but this is not the time when NO levels are highest. Note too that nothing is shown in
  terms of the sensitivity of $\Delta^{17}O$ to RO_2 concentration – i.e. calculated $\Delta^{17}O$ values are not
  directly compared with the calculated RO_2 concentrations.**

NO levels increase from 6:30 to 10:30 during SP 1 and SP 2, peak at around 10: 30 and then decrease.
We agree that the maximum is not reach exactly at 10:30 but somewhere between 10:00 and 11:00
because the given average NO mixing ratio represents the average of 1 min measurements between
10:00 and 11:00. Still, if the denuder sampling periods are used (7:30-10:30 and 10:30-13:30), the
highest average NO is between 7:30-10:30 because NO mixing ratio drops sharply from 11:00 onwards.
In addition, we explicitly state that this is the contribution of RO_2 and not its concentration. The section
has been reworded for greater clarity in the revised manuscript (see the revised Section 3.2 in our
response above).

- **Line 440: rephrase to "be used to improve understanding of the oxidation processes …"**

Thank you for pointing this out, which has been reworded accordingly in the revised manuscript.

- **Line 458: $\Delta^{17}O$-NO_2 should be $\Delta^{17}O$-NO_3 here (with the subscript NO_2+O_3)**

Thank you for pointing this mistake out, the sentence has been reworded in the revised manuscript as
(line 464):

"We think that our method may be very valuable in deciphering oxidation processes of N_r species, down to sub-
daily temporal scales."

- **Line 471: the formatting for the $\Delta^{17}O$ changes here**

Indeed, this is because this Δ symbolises a difference between the two same quantities, $\Delta^{17}O(NO_3^-{}_{calc})$
and $\Delta^{17}O(NO_3^-{}_{obs})$, while Δ symbolises the deviation of $\delta^{17}O$ to a reference value ($0.52 \times \delta^{17}O$).

- **Line 497: "in" should be "on" average**

Thank you for pointing this mistake out, which has been corrected accordingly in the revised manuscript.

- **Line 498: add were as in "values were more homogenous"**

Thank you for pointing this mistake out, the sentence has been reworded in the revised manuscript as (line 581):

"In summer, the $\Delta^{17}O(NO_3^-)$ values at the three altitudes were very similar."

- **Line 499: "attitude" should be "altitude"**

Thank you for pointing this mistake out, which has been corrected in the revised manuscript.

- **Line 525: "informations" should be "information"**

Thank you for pointing this mistake out, which has been corrected accordingly in the revised manuscript.

- **Line 564: the overall mean value stated here does not match what is in the Table.**

This is because is it the mean over GP #1 and GP #2, this information has been added to the in the revised manuscript for more clarity.

- **Line 585: Different papers seems to use different values for biomass combustion. Looking back at Fibiger and Hastings, 2016 the results indicate that latitudinal difference in $\delta^{15}N$ biomass exist and thus so should latitudinal difference in $\delta^{15}N$-NO from this source. Is that how Martinelli et al., 1999 is being used here? Please explain the values used if they do not directly represent the citations.**

We thank you for pointing this out and apologise for any lack of clarity. Similar to the choice of $\delta^{15}N$ of traffic emission, choosing a $\delta^{15}N$ for biomass burning is not straightforward regarding the variability observed in different studies. This is primarily due to the type of wood burnt. Our approach, which we agree is sorely lacking in detail in the initial manuscript, was to use an empirical relationship reported by Fibiger and Hastings (2016) between $\delta^{15}N(NO_x)$ emitted by biomass combustion and the $\delta^{15}N$ of the burnt vegetation: $\delta^{15}N(NO_x) = 0.98 \times \delta^{15}N_{biomass} + 1.7$. Regarding the $\delta^{15}N_{biomass}$ value, we decided to

take the average value given by Martinelli et al. (1999), (-2.8 ± 2.0) ‰ which represents an average over a large number of $\delta^{15}N$ measured in temperate forests.

However, following your comment, we would like to mention a more recent study, Chai et al. (2019), which is very similar to that of Fibiger and Hastings (2016). They confirmed the close linear relationship between biomass combustion $\delta^{15}N(NO_x)$ and $\delta^{15}N_{biomass}$, and combined their work with that of Fibiger and Hastings (2016) to obtain a new linear relationship, namely: $\delta^{15}N(NO_x) = (0.42 \pm 0.17) \times \delta^{15}N_{biomass} + 1.3$. Therefore, in order to account for more recent studies, we propose to use this relationship to derive a new mean value of biomass combustion $\delta^{15}N(NO_x)$, which is now at (0.1 ± 1.3) ‰, which is anyway very close to our initial value. More details are given in the revised manuscript as (lines 689-693):

"$\delta^{15}N$ of NO_x released during biomass combustion is primarily driven by the $\delta^{15}N$ of the biomass burnt (Fibiger and Hastings, 2016). We estimate an average $\delta^{15}N$ of biomass combustion NO_x at (-0.1 ± 1.3) ‰, using the empirical relationship of Chai et al. (2019) (which was derived from combustions of several North American wood species) and an average $\delta^{15}N$ of biomass at (-2.8 ± 2.0) ‰ representative of temperate forests (Martinelli et al., 1999)."

- **Line 627: what is the meaning of "faction" here?**

Thank you for pointing this out, this is a typing mistake of the word "factor". This section has been reworded in the revised manuscript for more clarity as (lines 741-744):

"Neglecting KIE associated with the N_2O_5 pathway and using the expression of the EIE fractionation factor between N_2O_5 and NO_2 given by Walters and Michalski (2015) (Appendix D) constrained with the mean nighttime temperature at our site, the isotopic composition of NO_3^- is expected be enriched in ^{15}N by about 29 ‰ compared to NO_2 . This estimated ^{15}N enrichment is about three times higher than the observed $\Delta^{15}(NO_3^- - NO_2)$ at our site."

- **Line 635: rephrase to "associated with a KIE effect…"**

Thank you for pointing this mistake out, which has been corrected in the revised manuscript.

- **Line 637: rephrase to "with the OH pathway"**

Thank you for pointing this mistake out, which has been corrected in the revised manuscript.

References

Albertin, S., Savarino, J., Bekki, S., Barbero, A., and Caillon, N.: Measurement report: Nitrogen isotopes (δ^{15}N) and first quantification of oxygen isotope anomalies (Δ^{17}O, δ^{18}O) in atmospheric nitrogen dioxide, Atmospheric Chemistry and Physics, 21, 10477–10497, https://doi.org/10.5194/acp-21-10477-2021, 2021.

Alexander, B., Hastings, M. G., Allman, D. J., Dachs, J., Thornton, J. A., and Kunasek, S. A.: Quantifying atmospheric nitrate formation pathways based on a global model of the oxygen isotopic composition (Δ^{17}O) of atmospheric nitrate, Atmospheric Chemistry and Physics, 9, 5043–5056, https://doi.org/10.5194/acp-9-5043-2009, 2009.

Alexander, B., Sherwen, T., Holmes, C. D., Fisher, J. A., Chen, Q., Evans, M. J., and Kasibhatla, P.: Global inorganic nitrate production mechanisms: comparison of a global model with nitrate isotope observations, Atmospheric Chemistry and Physics, 20, 3859–3877, https://doi.org/10.5194/acp-20-3859-2020, 2020.

Alicke, B., Geyer, A., Hofzumahaus, A., Holland, F., Konrad, S., Pätz, H. W., Schäfer, J., Stutz, J., Volz-Thomas, A., and Platt, U.: OH formation by HONO photolysis during the BERLIOZ experiment, Journal of Geophysical Research: Atmospheres, 108, PHO 3-1-PHO 3-17, https://doi.org/10.1029/2001JD000579, 2003.

Allard, J.: Qualité de l'air dans la Vallée de l'Arve : météorologie locale et mesures des réductions des émissions liées au chauffage au bois, PhD Thesis, Université Grenoble Alpes, 2018.

Ammann, M., Siegwolf, R., Pichlmayer, F., Suter, M., Saurer, M., and Brunold, C.: Estimating the uptake of trafic-derived NO_2 from ^{15}N abundance in Norway spruce needles, Oecologia, 118, 124–131, https://doi.org/10.1007/s004420050710, 1999.

Appel, B. R., Wall, S. M., Tokiwa, Y., and Haik, M.: Simultaneous nitric acid, particulate nitrate and acidity measurements in ambient air, Atmospheric Environment (1967), 14, 549–554, https://doi.org/10.1016/0004-6981(80)90084-0, 1980.

Appel, B. R., Tokiwa, Y., and Haik, M.: Sampling of nitrates in ambient air, Atmospheric Environment (1967), 15, 283–289, https://doi.org/10.1016/0004-6981(81)90029-9, 1981.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I - gas phase reactions of O_x, HO_x, NO_x and SO_x species, Atmospheric Chemistry and Physics, 4, 1461–1738, https://doi.org/10.5194/acp-4-1461-2004, 2004.

Aumont, B., Chervier, F., and Laval, S.: Contribution of HONO sources to the NOx/HOx/O3 chemistry in the polluted boundary layer, Atmospheric Environment, 37, 487–498, https://doi.org/10.1016/S1352-2310(02)00920-2, 2003.

Barkan, E. and Luz, B.: High-precision measurements of ^{17}O/^{16}O and ^{18}O/^{16}O of O_2 and O_2/Ar ratio in air, Rapid Commun. Mass Spectrom., 17, 2809–2814, https://doi.org/10.1002/rcm.1267, 2003.

Bauer, S. E., Koch, D., Unger, N., Metzger, S. M., Shindell, D. T., and Streets, D. G.: Nitrate aerosols today and in 2030: a global simulation including aerosols and tropospheric ozone, Atmos. Chem. Phys., 7, 5043–5059, https://doi.org/10.5194/acp-7-5043-2007, 2007.

Bekker, C., Walters, W. W., Murray, L. T., and Hastings, M. G.: Nitrate chemistry in the northeast US – Part 1: Nitrogen isotope seasonality tracks nitrate formation chemistry, Atmospheric Chemistry and Physics, 23, 4185–4201, https://doi.org/10.5194/acp-23-4185-2023, 2023.

Berhanu, T. A., Savarino, J., Bhattacharya, S. K., and Vicars, W. C.: ^{17}O excess transfer during the $NO_2 + O_3 \rightarrow NO_3 + O_2$ reaction, The Journal of Chemical Physics, 136, 044311, https://doi.org/10.1063/1.3666852, 2012.

Brown, S. S.: Variability in Nocturnal Nitrogen Oxide Processing and Its Role in Regional Air Quality, Science, 311, 67–70, https://doi.org/10.1126/science.1120120, 2006.

Brown, S. S. and Stutz, J.: Nighttime radical observations and chemistry, Chem Soc Rev, 41, 6405–6447, https://doi.org/10.1039/c2cs35181a, 2012.

Brown, S. S., Dubé, W. P., Peischl, J., Ryerson, T. B., Atlas, E., Warneke, C., de Gouw, J. A., te Lintel Hekkert, S., Brock, C. A., Flocke, F., Trainer, M., Parrish, D. D., Feshenfeld, F. C., and Ravishankara, A. R.: Budgets for nocturnal VOC oxidation by nitrate radicals aloft during the 2006 Texas Air Quality Study, Journal of Geophysical Research: Atmospheres, 116, https://doi.org/10.1029/2011JD016544, 2011.

Brulfert, G., Chemel, C., Chaxel, E., and Chollet, J. P.: Modelling photochemistry in alpine valleys, Atmos. Chem. Phys., 2005.

Chai, J., Miller, D. J., Scheuer, E., Dibb, J., Selimovic, V., Yokelson, R., Zarzana, K. J., Brown, S. S., Koss, A. R., Warneke, C., and Hastings, M.: Isotopic characterization of nitrogen oxides (NO_x), nitrous acid (HONO), and nitrate (pNO_3^-) from laboratory biomass burning during FIREX, Atmospheric Measurement Techniques, 12, 6303–6317, https://doi.org/10.5194/amt-12-6303-2019, 2019.

Chan, Y.-C., Evans, M. J., He, P., Holmes, C. D., Jaeglé, L., Kasibhatla, P., Liu, X.-Y., Sherwen, T., Thornton, J. A., Wang, X., Xie, Z., Zhai, S., and Alexander, B.: Heterogeneous Nitrate Production Mechanisms in Intense Haze Events in the North China Plain, Journal of Geophysical Research: Atmospheres, 126, e2021JD034688, https://doi.org/10.1029/2021JD034688, 2021.

Chang, Y., Zhang, Y., Tian, C., Zhang, S., Ma, X., Cao, F., Liu, X., Zhang, W., Kuhn, T., and Lehmann, M. F.: Nitrogen isotope fractionation during gas-to-particle conversion of NO_x to NO_3^- in the atmosphere – implications for isotope-based NO_x source apportionment, Atmospheric Chemistry and Physics, 18, 11647–11661, https://doi.org/10.5194/acp-18-11647-2018, 2018.

Chazette, P., Couvert, P., Randriamiarisoa, H., Sanak, J., Bonsang, B., Moral, P., Berthier, S., Salanave, S., and Toussaint, F.: Three-dimensional survey of pollution during winter in French Alps valleys, Atmospheric Environment, 39, 1035–1047, https://doi.org/10.1016/j.atmosenv.2004.10.014, 2005.

Chevrier, F.: Chauffage au bois et qualité de l'air en Vallée de l'Arve: définition d'un système de surveillance et impact d'une politique de rénovation du parc des appareils anciens, PhD-Thesis, Université Grenoble Alpes, 2016.

Crutzen, P. J.: The Role of NO and NO_2 in the Chemistry of the Troposphere and Stratosphere, Annu. Rev. Earth Planet. Sci., 7, 443–472, https://doi.org/10.1146/annurev.ea.07.050179.002303, 1979.

Dentener, F. J. and Crutzen, P. J.: Reaction of N2O5 on tropospheric aerosols: Impact on the global distributions of NO x , O3, and OH, Journal of Geophysical Research: Atmospheres, 98, 7149–7163, https://doi.org/10.1029/92JD02979, 1993.

Dubey, M. K., Mohrschladt, R., Donahue, N. M., and Anderson, J. G.: Isotope Specific Kinetics of Hydroxyl Radical (OH) with Water (H_2O): Testing Models of Reactivity and Atmospheric Fractionation, J. Phys. Chem. A, 101, 1494–1500, https://doi.org/10.1021/jp962332p, 1997.

Edwards, P. M., Brown, S. S., Roberts, J. M., Ahmadov, R., Banta, R. M., deGouw, J. A., Dubé, W. P., Field, R. A., Flynn, J. H., Gilman, J. B., Graus, M., Helmig, D., Koss, A., Langford, A. O., Lefer, B. L., Lerner, B. M., Li, R., Li, S.-M., McKeen, S. A., Murphy, S. M., Parrish, D. D., Senff, C. J., Soltis, J., Stutz, J., Sweeney, C., Thompson, C. R., Trainer, M. K., Tsai, C., Veres, P. R., Washenfelder, R. A., Warneke, C., Wild, R. J., Young, C. J., Yuan, B., and Zamora, R.: High winter ozone pollution from carbonyl photolysis in an oil and gas basin, Nature, 514, 351–354, https://doi.org/10.1038/nature13767, 2014.

Elliott, E. M., Yu, Z., Cole, A. S., and Coughlin, J. G.: Isotopic advances in understanding reactive nitrogen deposition and atmospheric processing, Science of The Total Environment, 662, 393–403, https://doi.org/10.1016/j.scitotenv.2018.12.177, 2019.

Elshorbany, Y. F., Kurtenbach, R., Wiesen, P., Lissi, E., Rubio, M., Villena, G., Gramsch, E., Rickard, A. R., Pilling, M. J., and Kleffmann, J.: Oxidation capacity of the city air of Santiago, Chile, Atmospheric Chemistry and Physics, 9, 2257–2273, https://doi.org/10.5194/acp-9-2257-2009, 2009.

Emmerson, K. M., Carslaw, N., Carpenter, L. J., Heard, D. E., Lee, J. D., and Pilling, M. J.: Urban Atmospheric Chemistry During the PUMA Campaign 1: Comparison of Modelled OH and HO_2 Concentrations with Measurements, J Atmos Chem, 52, 143–164, https://doi.org/10.1007/s10874-005-1322-3, 2005.

Fan, M.-Y., Zhang, Y.-L., Lin, Y.-C., Chang, Y.-H., Cao, F., Zhang, W.-Q., Hu, Y.-B., Bao, M.-Y., Liu, X.-Y., Zhai, X.-Y., Lin, X., Zhao, Z.-Y., and Song, W.-H.: Isotope-based source apportionment of nitrogen-containing aerosols: A case study in an industrial city in China, Atmospheric Environment, 212, 96–105, https://doi.org/10.1016/j.atmosenv.2019.05.020, 2019.

Fan, M.-Y., Zhang, Y.-L., Lin, Y.-C., Hong, Y., Zhao, Z.-Y., Xie, F., Du, W., Cao, F., Sun, Y., and Fu, P.: Important Role of NO_3 Radical to Nitrate Formation Aloft in Urban Beijing: Insights from Triple Oxygen Isotopes Measured at the Tower, Environ. Sci. Technol., 56, 6870–6879, https://doi.org/10.1021/acs.est.1c02843, 2022.

Fan, M.-Y., Zhang, W., Zhang, Y.-L., Li, J., Fang, H., Cao, F., Yan, M., Hong, Y., Guo, H., and Michalski, G.: Formation Mechanisms and Source Apportionments of Nitrate Aerosols in a Megacity of Eastern China Based On

Multiple Isotope Observations, Journal of Geophysical Research: Atmospheres, 128, e2022JD038129, https://doi.org/10.1029/2022JD038129, 2023.

Felix, J. D. and Elliott, E. M.: Isotopic composition of passively collected nitrogen dioxide emissions: Vehicle, soil and livestock source signatures, Atmospheric Environment, 92, 359–366, https://doi.org/10.1016/j.atmosenv.2014.04.005, 2014.

Felix, J. D., Elliott, E. M., and Shaw, S. L.: Nitrogen Isotopic Composition of Coal-Fired Power Plant NO_x: Influence of Emission Controls and Implications for Global Emission Inventories, Environ. Sci. Technol., 46, 3528–3535, https://doi.org/10.1021/es203355v, 2012.

Fibiger, D. L. and Hastings, M. G.: First Measurements of the Nitrogen Isotopic Composition of NO_x from Biomass Burning, Environ. Sci. Technol., 50, 11569–11574, https://doi.org/10.1021/acs.est.6b03510, 2016.

Finlayson-Pitts, B. J. and Pitts, J. N.: Chemistry of the Upper and Lower Atmosphere, Elsevier, https://doi.org/10.1016/B978-012257060-5/50003-4, 2000.

Frey, M. M., Savarino, J., Morin, S., Erbland, J., and Martins, J. M. F.: Photolysis imprint in the nitrate stable isotope signal in snow and atmosphere of East Antarctica and implications for reactive nitrogen cycling, Atmospheric Chemistry and Physics, 9, 8681–8696, https://doi.org/10.5194/acp-9-8681-2009, 2009.

Freyer, H. D.: Seasonal variation of $^{15}N/^{14}N$ ratios in atmospheric nitrate species, Tellus B, 43, 30–44, https://doi.org/10.1034/j.1600-0889.1991.00003.x, 1991.

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, Journal of Geophysical Research: Atmospheres, 98, 14791–14796, https://doi.org/10.1029/93JD00874, 1993.

Fu, X., Wang, T., Gao, J., Wang, P., Liu, Y., Wang, S., Zhao, B., and Xue, L.: Persistent Heavy Winter Nitrate Pollution Driven by Increased Photochemical Oxidants in Northern China, Environ. Sci. Technol., 54, 3881–3889, https://doi.org/10.1021/acs.est.9b07248, 2020.

Galloway, J. N., Townsend, A. R., Erisman, J. W., Bekunda, M., Cai, Z., Freney, J. R., Martinelli, L. A., Seitzinger, S. P., and Sutton, M. A.: Transformation of the Nitrogen Cycle: Recent Trends, Questions, and Potential Solutions, Science, 320, 889–892, https://doi.org/10.1126/science.1136674, 2008.

Geng, L., Alexander, B., Cole-Dai, J., Steig, E. J., Savarino, J., Sofen, E. D., and Schauer, A. J.: Nitrogen isotopes in ice core nitrate linked to anthropogenic atmospheric acidity change, Proc. Natl. Acad. Sci. U.S.A., 111, 5808–5812, https://doi.org/10.1073/pnas.1319441111, 2014.

Grannas, A. M., Jones, A. E., Dibb, J., Ammann, M., Anastasio, C., Beine, H. J., Bergin, M., Bottenheim, J., Boxe, C. S., Carver, G., Chen, G., Crawford, J. H., Dominé, F., Frey, M. M., Guzmán, M. I., Heard, D. E., Helmig, D., Hoffmann, M. R., Honrath, R. E., Huey, L. G., Hutterli, M., Jacobi, H. W., Klán, P., Lefer, B., McConnell, J., Plane, J., Sander, R., Savarino, J., Shepson, P. B., Simpson, W. R., Sodeau, J. R., von Glasow, R., Weller, R.,

Wolff, E. W., and Zhu, T.: An overview of snow photochemistry: evidence, mechanisms and impacts, Atmospheric Chemistry and Physics, 7, 4329–4373, https://doi.org/10.5194/acp-7-4329-2007, 2007.

Gu, P., Dallmann, T. R., Li, H. Z., Tan, Y., and Presto, A. A.: Quantifying Urban Spatial Variations of Anthropogenic VOC Concentrations and Source Contributions with a Mobile Sampling Platform, Int J Environ Res Public Health, 16, https://doi.org/10.3390/ijerph16091632, 2019.

Hastings, M. G., Jarvis, J. C., and Steig, E. J.: Anthropogenic Impacts on Nitrogen Isotopes of Ice-Core Nitrate, Science, 324, 1288–1288, https://doi.org/10.1126/science.1170510, 2009.

He, P., Xie, Z., Chi, X., Yu, X., Fan, S., Kang, H., Liu, C., and Zhan, H.: Atmospheric $\Delta^{17}O(NO_3^-)$ reveals nocturnal chemistry dominates nitrate production in Beijing haze, Atmospheric Chemistry and Physics, 18, 14465–14476, https://doi.org/10.5194/acp-18-14465-2018, 2018.

He, P., Xie, Z., Yu, X., Wang, L., Kang, H., and Yue, F.: The observation of isotopic compositions of atmospheric nitrate in Shanghai China and its implication for reactive nitrogen chemistry, Science of The Total Environment, 714, 136727, https://doi.org/10.1016/j.scitotenv.2020.136727, 2020.

Heaton, T. H. E.: $^{15}N/^{14}N$ ratios of NO_x from vehicle engines and coal-fired power stations, Tellus B, 42, 304–307, https://doi.org/10.1034/j.1600-0889.1990.00007.x-i1, 1990.

Hoesly, R. M., Smith, S. J., Feng, L., Klimont, Z., Janssens-Maenhout, G., Pitkanen, T., Seibert, J. J., Vu, L., Andres, R. J., Bolt, R. M., Bond, T. C., Dawidowski, L., Kholod, N., Kurokawa, J., Li, M., Liu, L., Lu, Z., Moura, M. C. P., O'Rourke, P. R., and Zhang, Q.: Historical (1750–2014) anthropogenic emissions of reactive gases and aerosols from the Community Emissions Data System (CEDS), Geoscientific Model Development, 11, 369–408, https://doi.org/10.5194/gmd-11-369-2018, 2018.

Holland, E. A., Dentener, F. J., Braswell, B. H., and Sulzman, J. M.: Contemporary and pre-industrial global reactive nitrogen budgets, Biogeochemistry, 46, 7–43, https://doi.org/10.1023/A:1006148011944, 1999.

Huang, R.-J., Zhang, Y., Bozzetti, C., Ho, K.-F., Cao, J.-J., Han, Y., Daellenbach, K. R., Slowik, J. G., Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A., Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z., Szidat, S., Baltensperger, U., Haddad, I. E., and Prévôt, A. S. H.: High secondary aerosol contribution to particulate pollution during haze events in China, Nature, 514, 218–222, https://doi.org/10.1038/nature13774, 2014.

Kanaya, Y., Cao, R., Akimoto, H., Fukuda, M., Komazaki, Y., Yokouchi, Y., Koike, M., Tanimoto, H., Takegawa, N., and Kondo, Y.: Urban photochemistry in central Tokyo: 1. Observed and modeled OH and HO_2 radical concentrations during the winter and summer of 2004, Journal of Geophysical Research: Atmospheres, 112, https://doi.org/10.1029/2007JD008670, 2007.

Kim, H., Walters, W. W., Bekker, C., Murray, L. T., and Hastings, M. G.: Nitrate chemistry in the northeast US – Part 2: Oxygen isotopes reveal differences in particulate and gas-phase formation, Atmospheric Chemistry and Physics, 23, 4203–4219, https://doi.org/10.5194/acp-23-4203-2023, 2023.

Kirchstetter, T. W., Harley, R. A., and Littlejohn, D.: Measurement of Nitrous Acid in Motor Vehicle Exhaust, Environ. Sci. Technol., 30, 2843–2849, https://doi.org/10.1021/es960135y, 1996.

Kurtenbach, R., Becker, K. H., Gomes, J. A. G., Kleffmann, J., Lörzer, J. C., Spittler, M., Wiesen, P., Ackermann, R., Geyer, A., and Platt, U.: Investigations of emissions and heterogeneous formation of HONO in a road traffic tunnel, Atmospheric Environment, 35, 3385–3394, https://doi.org/10.1016/S1352-2310(01)00138-8, 2001.

Largeron, Y. and Staquet, C.: Persistent inversion dynamics and wintertime PM_{10} air pollution in Alpine valleys, Atmospheric Environment, 135, 92–108, https://doi.org/10.1016/j.atmosenv.2016.03.045, 2016.

Legrand, M., Preunkert, S., Wolff, E., Weller, R., Jourdain, B., and Wagenbach, D.: Year-round records of bulk and size-segregated aerosol composition in central Antarctica (Concordia site) – Part 1: Fractionation of sea-salt particles, Atmospheric Chemistry and Physics, 17, 14039–14054, https://doi.org/10.5194/acp-17-14039-2017, 2017.

Leighton, P. A.: Photochemistry of Air Pollution., 66, 1961.

Li, J., Zhang, X., Orlando, J., Tyndall, G., and Michalski, G.: Quantifying the nitrogen isotope effects during photochemical equilibrium between NO and NO_2: implications for $\delta^{15}N$ in tropospheric reactive nitrogen, Atmospheric Chemistry and Physics, 20, 9805–9819, https://doi.org/10.5194/acp-20-9805-2020, 2020.

Li, J., Davy, P., Harvey, M., Katzman, T., Mitchell, T., and Michalski, G.: Nitrogen isotopes in nitrate aerosols collected in the remote marine boundary layer: Implications for nitrogen isotopic fractionations among atmospheric reactive nitrogen species, Atmospheric Environment, 245, 118028, https://doi.org/10.1016/j.atmosenv.2020.118028, 2021a.

Li, K., Jacob, D. J., Liao, H., Qiu, Y., Shen, L., Zhai, S., Bates, K. H., Sulprizio, M. P., Song, S., Lu, X., Zhang, Q., Zheng, B., Zhang, Y., Zhang, J., Lee, H. C., and Kuk, S. K.: Ozone pollution in the North China Plain spreading into the late-winter haze season, Proceedings of the National Academy of Sciences, 118, e2015797118, https://doi.org/10.1073/pnas.2015797118, 2021b.

Li, Z., Walters, W. W., Hastings, M. G., Song, L., Huang, S., Zhu, F., Liu, D., Shi, G., Li, Y., and Fang, Y.: Atmospheric nitrate formation pathways in urban and rural atmosphere of Northeast China: Implications for complicated anthropogenic effects, Environmental Pollution, 296, 118752, https://doi.org/10.1016/j.envpol.2021.118752, 2022.

Lim, S., Lee, M., Savarino, J., and Laj, P.: Oxidation pathways and emission sources of atmospheric particulate nitrate in Seoul: based on $\delta^{15}N$ and $\Delta^{17}O$ measurements, Atmospheric Chemistry and Physics, 22, 5099–5115, https://doi.org/10.5194/acp-22-5099-2022, 2022.

Liu, J., Liu, Z., Ma, Z., Yang, S., Yao, D., Zhao, S., Hu, B., Tang, G., Sun, J., Cheng, M., Xu, Z., and Wang, Y.: Detailed budget analysis of HONO in Beijing, China: Implication on atmosphere oxidation capacity in polluted megacity, Atmospheric Environment, 244, 117957, https://doi.org/10.1016/j.atmosenv.2020.117957, 2021.

Liu, Z., Hu, K., Zhang, K., Zhu, S., Wang, M., and Li, L.: VOCs sources and roles in O3 formation in the central Yangtze River Delta region of China, Atmospheric Environment, 302, 119755, https://doi.org/10.1016/j.atmosenv.2023.119755, 2023.

Luo, L., Wu, S., Zhang, R., Wu, Y., Li, J., and Kao, S.: What controls aerosol δ15N-NO3−? NOx emission sources vs. nitrogen isotope fractionation, Science of The Total Environment, 871, 162185, https://doi.org/10.1016/j.scitotenv.2023.162185, 2023.

Martinelli, L. A., Piccolo, M. C., Townsend, A. R., Vitousek, P. M., Cuevas, E., McDowell, W., Robertson, G. P., Santos, O. C., and Treseder, K.: Nitrogen stable isotopic composition of leaves and soil: Tropical versus temperate forests, Biogeochemistry, 46, 45–65, https://doi.org/10.1023/A:1006100128782, 1999.

Masson-Delmotte, V., Zhai, A., Pirani, A., Connors, S. L., Péan, C., Berger, S., Caud, N., Chen, Y., Goldfarb, L., Gomis, M. I., Huang, M., Leitzell, K., Lonnoy, E., Matthews, J. B. R., Maycock, T. K., Waterfield, T., Yelekçi, O., Yu, R., and Zhou, B.: In Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 147–286, https://doi.org/10.1017/9781009157896.003, 2021.

Michalski, G., Scott, Z., Kabiling, M., and Thiemens, M. H.: First measurements and modeling of $\Delta^{17}O$ in atmospheric nitrate., Geophysical Research Letters, 30, 1870, https://doi.org/10.1029/2003GL017015, 2003.

Michalski, G., Bhattacharya, S. K., and Girsch, G.: NO_x cycle and the tropospheric ozone isotope anomaly: an experimental investigation, Atmospheric Chemistry and Physics, 14, 4935–4953, https://doi.org/10.5194/acp-14-4935-2014, 2014.

Michoud, V., Colomb, A., Borbon, A., Miet, K., Beekmann, M., Camredon, M., Aumont, B., Perrier, S., Zapf, P., Siour, G., Ait-Helal, W., Afif, C., Kukui, A., Furger, M., Dupont, J. C., Haeffelin, M., and Doussin, J. F.: Study of the unknown HONO daytime source at a European suburban site during the MEGAPOLI summer and winter field campaigns, Atmospheric Chemistry and Physics, 14, 2805–2822, https://doi.org/10.5194/acp-14-2805-2014, 2014.

Michoud, V., Doussin, J.-F., Colomb, A., Afif, C., Borbon, A., Camredon, M., Aumont, B., Legrand, M., and Beekmann, M.: Strong HONO formation in a suburban site during snowy days, Atmospheric Environment, 116, 155–158, https://doi.org/10.1016/j.atmosenv.2015.06.040, 2015.

Miller, C. E. and Yung, Y. L.: Photo-induced isotopic fractionation, Journal of Geophysical Research: Atmospheres, 105, 29039–29051, https://doi.org/10.1029/2000JD900388, 2000.

Miller, D. J., Wojtal, P. K., Clark, S. C., and Hastings, M. G.: Vehicle NO_x emission plume isotopic signatures: Spatial variability across the eastern United States, Journal of Geophysical Research: Atmospheres, 122, 4698–4717, https://doi.org/10.1002/2016JD025877, 2017.

Miller, D. J., Chai, J., Guo, F., Dell, C. J., Karsten, H., and Hastings, M. G.: Isotopic Composition of In Situ Soil NO_x Emissions in Manure-Fertilized Cropland, Geophysical Research Letters, 45, 12,058-12,066, https://doi.org/10.1029/2018GL079619, 2018.

Miller, J. A. and Bowman, C. T.: Mechanism and modeling of nitrogen chemistry in combustion, Progress in Energy and Combustion Science, 15, 287–338, https://doi.org/10.1016/0360-1285(89)90017-8, 1989.

Morin, S., Savarino, J., Bekki, S., Cavender, A., Shepson, P. B., and Bottenheim, J. W.: Major influence of BrO on the NO_3 and nitrate budgets in the Arctic spring, inferred from $\Delta^{17}O(NO_3^-)$ measurements during ozone depletion events, Environ. Chem., 4, 238, https://doi.org/10.1071/EN07003, 2007.

Morin, S., Savarino, J., Frey, M. M., Domine, F., Jacobi, H.-W., Kaleschke, L., and Martins, J. M. F.: Comprehensive isotopic composition of atmospheric nitrate in the Atlantic Ocean boundary layer from 65°S to 79°N, Journal of Geophysical Research: Atmospheres, 114, https://doi.org/10.1029/2008JD010696, 2009.

Morin, S., Sander, R., and Savarino, J.: Simulation of the diurnal variations of the oxygen isotope anomaly ($\Delta^{17}O$) of reactive atmospheric species, Atmospheric Chemistry and Physics, 11, 3653–3671, https://doi.org/10.5194/acp-11-3653-2011, 2011.

Newsome, B. and Evans, M.: Impact of uncertainties in inorganic chemical rate constants on tropospheric composition and ozone radiative forcing, Atmos. Chem. Phys., 17, 14333–14352, https://doi.org/10.5194/acp-17-14333-2017, 2017.

Olofson, K. F. G., Andersson, P. U., Hallquist, M., Ljungström, E., Tang, L., Chen, D., and Pettersson, J. B. C.: Urban aerosol evolution and particle formation during wintertime temperature inversions, Atmospheric Environment, 43, 340–346, https://doi.org/10.1016/j.atmosenv.2008.09.080, 2009.

Park, R. J., Jacob, D. J., Field, B. D., Yantosca, R. M., and Chin, M.: Natural and transboundary pollution influences on sulfate-nitrate-ammonium aerosols in the United States: Implications for policy, Journal of Geophysical Research: Atmospheres, 109, https://doi.org/10.1029/2003JD004473, 2004.

Patris, N., Cliff, S., Quinn, P., Kasem, M., and Thiemens, M.: Isotopic analysis of aerosol sulfate and nitrate during ITCT-2k2: Determination of different formation pathways as a function of particle size, Journal of Geophysical Research, 112, https://doi.org/10.1029/2005JD006214, 2007.

Penkett, S. A., Burgess, R. A., Coe, H., Coll, I., Hov, Ø., Lindskog, A., Schmidbauer, N., Solberg, S., Roemer, M., Thijsse, T., Beck, J., and Reeves, C. E.: Evidence for large average concentrations of the nitrate radical (NO_3) in Western Europe from the HANSA hydrocarbon database, Atmospheric Environment, 41, 3465–3478, https://doi.org/10.1016/j.atmosenv.2006.11.055, 2007.

Prabhakar, G., Parworth, C. L., Zhang, X., Kim, H., Young, D. E., Beyersdorf, A. J., Ziemba, L. D., Nowak, J. B., Bertram, T. H., Faloona, I. C., Zhang, Q., and Cappa, C. D.: Observational assessment of the role of nocturnal residual-layer chemistry in determining daytime surface particulate nitrate concentrations, Atmospheric Chemistry and Physics, 17, 14747–14770, https://doi.org/10.5194/acp-17-14747-2017, 2017.

Prospero, J. M. and Savoie, D. L.: Effect of continental sources on nitrate concentrations over the Pacific Ocean, Nature, 339, 687–689, https://doi.org/10.1038/339687a0, 1989.

Quimbayo-Duarte, J., Chemel, C., Staquet, C., Troude, F., and Arduini, G.: Drivers of severe air pollution events in a deep valley during wintertime: A case study from the Arve river valley, France, Atmospheric Environment, 247, 118030, https://doi.org/10.1016/j.atmosenv.2020.118030, 2021.

Ren, J., Guo, F., and Xie, S.: Diagnosing ozone–NO$_x$–VOC sensitivity and revealing causes of ozone increases in China based on 2013–2021 satellite retrievals, Atmos. Chem. Phys., 22, 15035–15047, https://doi.org/10.5194/acp-22-15035-2022, 2022.

Ren, X., Brune, W. H., Mao, J., Mitchell, M. J., Lesher, R. L., Simpas, J. B., Metcalf, A. R., Schwab, J. J., Cai, C., Li, Y., Demerjian, K. L., Felton, H. D., Boynton, G., Adams, A., Perry, J., He, Y., Zhou, X., and Hou, J.: Behavior of OH and HO$_2$ in the winter atmosphere in New York City, Atmospheric Environment, 40, 252–263, https://doi.org/10.1016/j.atmosenv.2005.11.073, 2006.

Savard, M. M., Cole, A. S., Vet, R., and Smirnoff, A.: The Δ^{17}O and δ^{18}O values of atmospheric nitrates simultaneously collected downwind of anthropogenic sources – implications for polluted air masses, Atmospheric Chemistry and Physics, 18, 10373–10389, https://doi.org/10.5194/acp-18-10373-2018, 2018.

Savarino, J., Kaiser, J., Morin, S., Sigman, D. M., and Thiemens, M. H.: Nitrogen and oxygen isotopic constraints on the origin of atmospheric nitrate in coastal Antarctica, Atmos. Chem. Phys., 21, 2007.

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, PNAS, 110, 17668–17673, https://doi.org/10.1073/pnas.1216639110, 2013.

Schaap, M., Müller, K., and ten Brink, H. M.: Constructing the European aerosol nitrate concentration field from quality analysed data, Atmospheric Environment, 36, 1323–1335, https://doi.org/10.1016/S1352-2310(01)00556-8, 2002.

Shah, V., Jaeglé, L., Thornton, J. A., Lopez-Hilfiker, F. D., Lee, B. H., Schroder, J. C., Campuzano-Jost, P., Jimenez, J. L., Guo, H., Sullivan, A. P., Weber, R. J., Green, J. R., Fiddler, M. N., Bililign, S., Campos, T. L., Stell, M., Weinheimer, A. J., Montzka, D. D., and Brown, S. S.: Chemical feedbacks weaken the wintertime response of particulate sulfate and nitrate to emissions reductions over the eastern United States, Proc Natl Acad Sci USA, 115, 8110–8115, https://doi.org/10.1073/pnas.1803295115, 2018.

Shi, X., Nenes, A., Xiao, Z., Song, S., Yu, H., Shi, G., Zhao, Q., Chen, K., Feng, Y., and Russell, A. G.: High-Resolution Data Sets Unravel the Effects of Sources and Meteorological Conditions on Nitrate and Its Gas-Particle Partitioning, Environ. Sci. Technol., 53, 3048–3057, https://doi.org/10.1021/acs.est.8b06524, 2019.

Simpson, W. R., Brown, S. S., Saiz-Lopez, A., Thornton, J. A., and von Glasow, R.: Tropospheric Halogen Chemistry: Sources, Cycling, and Impacts, Chem. Rev., 115, 4035–4062, https://doi.org/10.1021/cr5006638, 2015.

Song, W., Liu, X.-Y., Houlton, B. Z., and Liu, C.-Q.: Isotopic constraints confirm the significant role of microbial nitrogen oxides emissions from the land and ocean environment, National Science Review, 9, nwac106, https://doi.org/10.1093/nsr/nwac106, 2022.

Spataro, F., Ianniello, A., Esposito, G., Allegrini, I., Zhu, T., and Hu, M.: Occurrence of atmospheric nitrous acid in the urban area of Beijing (China), Science of The Total Environment, 447, 210–224, https://doi.org/10.1016/j.scitotenv.2012.12.065, 2013.

Stone, D., Whalley, L. K., and Heard, D. E.: Tropospheric OH and HO2 radicals: field measurements and model comparisons, Chem. Soc. Rev., 41, 6348–6404, https://doi.org/10.1039/C2CS35140D, 2012.

Tan, Z., Rohrer, F., Lu, K., Ma, X., Bohn, B., Broch, S., Dong, H., Fuchs, H., Gkatzelis, G. I., Hofzumahaus, A., Holland, F., Li, X., Liu, Y., Liu, Y., Novelli, A., Shao, M., Wang, H., Wu, Y., Zeng, L., Hu, M., Kiendler-Scharr, A., Wahner, A., and Zhang, Y.: Wintertime photochemistry in Beijing: observations of RO$_x$ radical concentrations in the North China Plain during the BEST-ONE campaign, Atmos. Chem. Phys., 18, 12391–12411, https://doi.org/10.5194/acp-18-12391-2018, 2018.

Thiemens, M. H.: History and Applications of Mass-independent Isotope Effects, Annual Review of Earth and Planetary Sciences, 34, 217–262, https://doi.org/10.1146/annurev.earth.34.031405.125026, 2006.

Thornton, J. A., Kercher, J. P., Riedel, T. P., Wagner, N. L., Cozic, J., Holloway, J. S., Dubé, W. P., Wolfe, G. M., Quinn, P. K., Middlebrook, A. M., Alexander, B., and Brown, S. S.: A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry, Nature, 464, 271–274, https://doi.org/10.1038/nature08905, 2010.

Tørseth, K., Aas, W., Breivik, K., Fjæraa, A. M., Fiebig, M., Hjellbrekke, A. G., Lund Myhre, C., Solberg, S., and Yttri, K. E.: Introduction to the European Monitoring and Evaluation Programme (EMEP) and observed atmospheric composition change during 1972-2009, Atmospheric Chemistry and Physics, 12, 5447–5481, https://doi.org/10.5194/acp-12-5447-2012, 2012.

Tsimpidi, A. P., Karydis, V. A., and Pandis, S. N.: Response of Fine Particulate Matter to Emission Changes of Oxides of Nitrogen and Anthropogenic Volatile Organic Compounds in the Eastern United States, Journal of the Air & Waste Management Association, 58, 1463–1473, https://doi.org/10.3155/1047-3289.58.11.1463, 2008.

Vicars, W. C. and Savarino, J.: Quantitative constraints on the ^{17}O-excess (Δ^{17}O) signature of surface ozone: Ambient measurements from 50°N to 50°S using the nitrite-coated filter technique, Geochimica et Cosmochimica Acta, 135, 270–287, https://doi.org/10.1016/j.gca.2014.03.023, 2014.

Vicars, W. C., Morin, S., Savarino, J., Wagner, N. L., Erbland, J., Vince, E., Martins, J. M. F., Lerner, B. M., Quinn, P. K., Coffman, D. J., Williams, E. J., and Brown, S. S.: Spatial and diurnal variability in reactive nitrogen oxide chemistry as reflected in the isotopic composition of atmospheric nitrate: Results from the CalNex 2010 field study, Journal of Geophysical Research: Atmospheres, 118, 10,567-10,588, https://doi.org/10.1002/jgrd.50680, 2013.

Vitousek, P. M., Aber, J. D., Howarth, R. W., Likens, G. E., Matson, P. A., Schindler, D. W., Schlesinger, W. H., and Tilman, D. G.: Human Alteration of the Global Nitrogen Cycle: Sources and Consequences, Ecological Applications, 7, 737–750, https://doi.org/10.1890/1051-0761(1997)007[0737:HAOTGN]2.0.CO;2, 1997.

Walters, W. W. and Michalski, G.: Theoretical calculation of nitrogen isotope equilibrium exchange fractionation factors for various NO_y molecules, Geochimica et Cosmochimica Acta, 164, 284–297, https://doi.org/10.1016/j.gca.2015.05.029, 2015.

Walters, W. W. and Michalski, G.: Theoretical calculation of oxygen equilibrium isotope fractionation factors involving various NO_y molecules, OH, and H_2O and its implications for isotope variations in atmospheric nitrate, Geochimica et Cosmochimica Acta, 191, 89–101, https://doi.org/10.1016/j.gca.2016.06.039, 2016.

Walters, W. W., Tharp, B. D., Fang, H., Kozak, B. J., and Michalski, G.: Nitrogen isotope composition of thermally produced NO_x from various fossil-fuel combustion sources, Environmental Science & Technology, 49, 11363–11371, https://doi.org/10.1021/acs.est.5b02769, 2015a.

Walters, W. W., Goodwin, S. R., and Michalski, G.: Nitrogen Stable Isotope Composition ($\delta^{15}N$) of Vehicle-Emitted NO_x, Environ. Sci. Technol., 49, 2278–2285, https://doi.org/10.1021/es505580v, 2015b.

Walters, W. W., Simonini, D. S., and Michalski, G.: Nitrogen isotope exchange between NO and NO_2 and its implications for $\delta^{15}N$ variations in tropospheric NO_x and atmospheric nitrate, Geophysical Research Letters, 43, 440–448, https://doi.org/10.1002/2015GL066438, 2016.

Walters, W. W., Fang, H., and Michalski, G.: Summertime diurnal variations in the isotopic composition of atmospheric nitrogen dioxide at a small midwestern United States city, Atmospheric Environment, 179, 1–11, https://doi.org/10.1016/j.atmosenv.2018.01.047, 2018.

Wang, X., Jacob, D. J., Eastham, S. D., Sulprizio, M. P., Zhu, L., Chen, Q., Alexander, B., Sherwen, T., Evans, M. J., Lee, B. H., Haskins, J. D., Lopez-Hilfiker, F. D., Thornton, J. A., Huey, G. L., and Liao, H.: The role of chlorine in global tropospheric chemistry, Atmospheric Chemistry and Physics, 19, 3981–4003, https://doi.org/10.5194/acp-19-3981-2019, 2019a.

Wang, Y., Zhang, Q. Q., He, K., Zhang, Q., and Chai, L.: Sulfate-nitrate-ammonium aerosols over China: response to 2000–2015 emission changes of sulfur dioxide, nitrogen oxides, and ammonia, Atmospheric Chemistry and Physics, 13, 2635–2652, https://doi.org/10.5194/acp-13-2635-2013, 2013.

Wang, Y., Gao, W., Wang, S., Song, T., Gong, Z., Ji, D., Wang, L., Liu, Z., Tang, G., Huo, Y., Tian, S., Li, J., Li, M., Yang, Y., Chu, B., Petäjä, T., Kerminen, V.-M., He, H., Hao, J., Kulmala, M., Wang, Y., and Zhang, Y.: Contrasting trends of $PM_{2.5}$ and surface-ozone concentrations in China from 2013 to 2017, National Science Review, 7, 1331–1339, https://doi.org/10.1093/nsr/nwaa032, 2020.

Wang, Y., Liu, J., Jiang, F., Chen, Z., Wu, L., Zhou, S., Pei, C., Kuang, Y., Cao, F., Zhang, Y., Fan, M., Zheng, J., Li, J., and Zhang, G.: Vertical measurements of stable nitrogen and oxygen isotope composition of fine particulate nitrate aerosol in Guangzhou city: Source apportionment and oxidation pathway, Science of The Total Environment, 865, 161239, https://doi.org/10.1016/j.scitotenv.2022.161239, 2023.

Wang, Y. L., Song, W., Yang, W., Sun, X. C., Tong, Y. D., Wang, X. M., Liu, C. Q., Bai, Z. P., and Liu, Z. Y.: Influences of Atmospheric Pollution on the Contributions of Major Oxidation Pathways to $PM_{2.5}$ Nitrate Formation in Beijing, Journal of Geophysical Research: Atmospheres, 124, 4174–4185, https://doi.org/10.1029/2019JD030284, 2019b.

Wayne, R. P., Barnes, I., Biggs, P., Burrows, J. P., Canosa-Mas, C. E., Hjorth, J., Le Bras, G., Moortgat, G. K., Perner, D., Poulet, G., Restelli, G., and Sidebottom, H.: The nitrate radical: Physics, chemistry, and the atmosphere, Atmospheric Environment. Part A. General Topics, 25, 1–203, https://doi.org/10.1016/0960-1686(91)90192-A, 1991.

WHO: Whorld Health Organization global air quality guidelines: particulate matter ($PM_{2.5}$ and PM_{10}), ozone, nitrogen dioxide, sulfur dioxide and carbon monoxide, 2021.

Xue, C.: Substantially Growing Interest in the Chemistry of Nitrous Acid (HONO) in China: Current Achievements, Problems, and Future Directions, Environ. Sci. Technol., 56, 7375–7377, https://doi.org/10.1021/acs.est.2c02237, 2022.

Xue, C., Ye, C., Kleffmann, J., Zhang, W., He, X., Liu, P., Zhang, C., Zhao, X., Liu, C., Ma, Z., Liu, J., Wang, J., Lu, K., Catoire, V., Mellouki, A., and Mu, Y.: Atmospheric measurements at Mt. Tai – Part II: HONO budget and radical (RO_x + NO_3) chemistry in the lower boundary layer, Atmospheric Chemistry and Physics, 22, 1035–1057, https://doi.org/10.5194/acp-22-1035-2022, 2022.

Ye, C., Lu, K., Ma, X., Qiu, W., Li, S., Yang, X., Xue, C., Zhai, T., Liu, Y., Li, X., Li, Y., Wang, H., Tan, Z., Chen, X., Dong, H., Zeng, L., Hu, M., and Zhang, Y.: HONO chemistry at a suburban site during the EXPLORE-YRD campaign in 2018: HONO formation mechanisms and impacts on O_3 production, EGUsphere, 1–41, https://doi.org/10.5194/egusphere-2023-1058, 2023.

Young, E. D., Galy, A., and Nagahara, H.: Kinetic and equilibrium mass-dependent isotope fractionation laws in nature and their geochemical and cosmochemical significance, Geochimica et Cosmochimica Acta, 66, 1095–1104, https://doi.org/10.1016/S0016-7037(01)00832-8, 2002.

Yu, Z. and Elliott, E. M.: Novel Method for Nitrogen Isotopic Analysis of Soil-Emitted Nitric Oxide, Environ. Sci. Technol., 51, 6268–6278, https://doi.org/10.1021/acs.est.7b00592, 2017.

Zhang, R., Wang, G., Guo, S., Zamora, M. L., Ying, Q., Lin, Y., Wang, W., Hu, M., and Wang, Y.: Formation of Urban Fine Particulate Matter, Chem. Rev., 115, 3803–3855, https://doi.org/10.1021/acs.chemrev.5b00067, 2015.

Zhang, W., Bi, X., Zhang, Y., Wu, J., and Feng, Y.: Diesel vehicle emission accounts for the dominate NO_x source to atmospheric particulate nitrate in a coastal city: Insights from nitrate dual isotopes of $PM_{2.5}$, Atmospheric Research, 278, 106328, https://doi.org/10.1016/j.atmosres.2022.106328, 2022a.

Zhang, Y.-L., Zhang, W., Fan, M.-Y., Li, J., Fang, H., Cao, F., Lin, Y.-C., Wilkins, B. P., Liu, X., Bao, M., Hong, Y., and Michalski, G.: A diurnal story of $\Delta^{17}O(NO_3^-)$ in urban Nanjing and its implication for nitrate aerosol formation, npj Clim Atmos Sci, 5, 1–10, https://doi.org/10.1038/s41612-022-00273-3, 2022b.

Zhou, W., Gao, M., He, Y., Wang, Q., Xie, C., Xu, W., Zhao, J., Du, W., Qiu, Y., Lei, L., Fu, P., Wang, Z., Worsnop, D. R., Zhang, Q., and Sun, Y.: Response of aerosol chemistry to clean air action in Beijing, China: Insights from two-year ACSM measurements and model simulations, Environmental Pollution, 255, 113345, https://doi.org/10.1016/j.envpol.2019.113345, 2019.

Zong, Z., Wang, X., Tian, C., Chen, Y., Fang, Y., Zhang, F., Li, C., Sun, J., Li, J., and Zhang, G.: First Assessment of NOx Sources at a Regional Background Site in North China Using Isotopic Analysis Linked with Modeling, Environmental Science and Technology, 51, 5923–5931, https://doi.org/10.1021/acs.est.6b06316, 2017.

Zong, Z., Sun, Z., Xiao, L., Tian, C., Liu, J., Sha, Q., Li, J., Fang, Y., Zheng, J., and Zhang, G.: Insight into the Variability of the Nitrogen Isotope Composition of Vehicular NO_x in China, Environ. Sci. Technol., acs.est.0c04749, https://doi.org/10.1021/acs.est.0c04749, 2020.