

## **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>.**

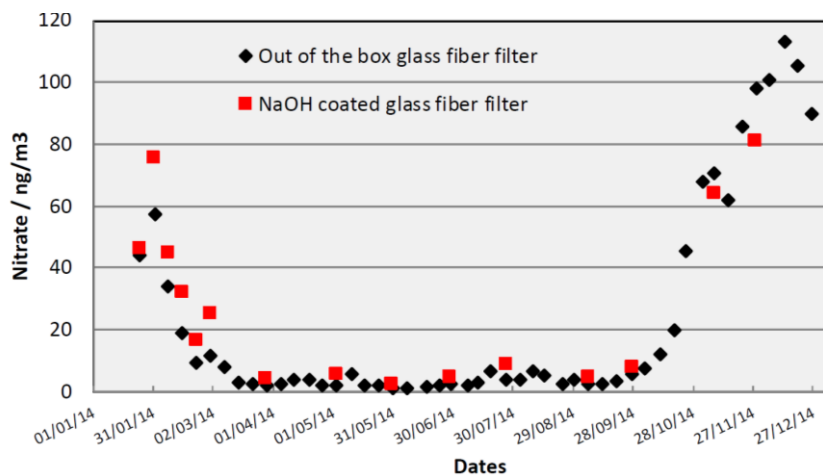
These two publications are now referenced in the manuscript as additional data for comparisons. However, please note that, although these measurements are generally in agreement with our results, these two studies collected nitrate on a weekly basis with gas and particulate phase segregation for nitrate 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<sub>3</sub> and particle phase nitrate are quantitatively 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).**

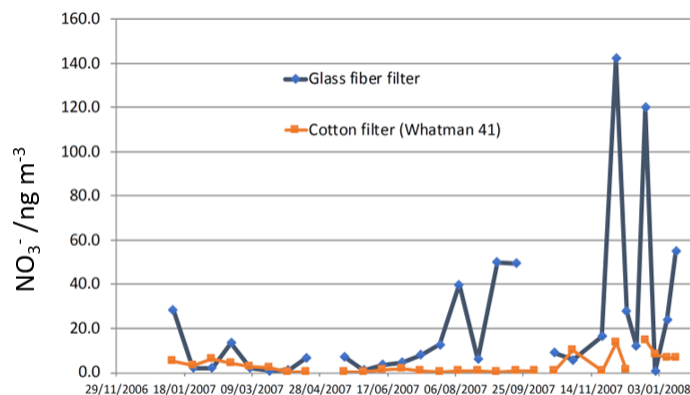
Regardless of the type of filter substrate, determining the exact nature of the nitrate collected on filter samples has always been a matter of debate, and no medium can completely prevent sampling artefacts

(e.g., Schaap et al., 2002; Appel et al., 1980). For instance, nitric acid ( $\text{HNO}_3$ ) can potentially be absorbed on aerosols that have already deposited on the filter material. In addition,  $\text{HNO}_3$  can evaporate from the filter after exposure. We recognise that the references cited do not prove that glass fibre filters effectively collect both  $\text{HNO}_3$  and particulate nitrate ( $p\text{-NO}_3^-$ ), but only assume that the ambient conditions (i.e., marine boundary layer and therefore the presence of sea salts) allow effective collection of  $\text{HNO}_3$ , 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  $\text{HNO}_3$  is collected quantitatively on the glass fibre filters due to their NaCl coating, which has been shown in the literature to collect  $\text{HNO}_3$  (Appel et al., 1981). If you wish, we can share the IC analyses of virgin filters, which prove the high NaCl loading.

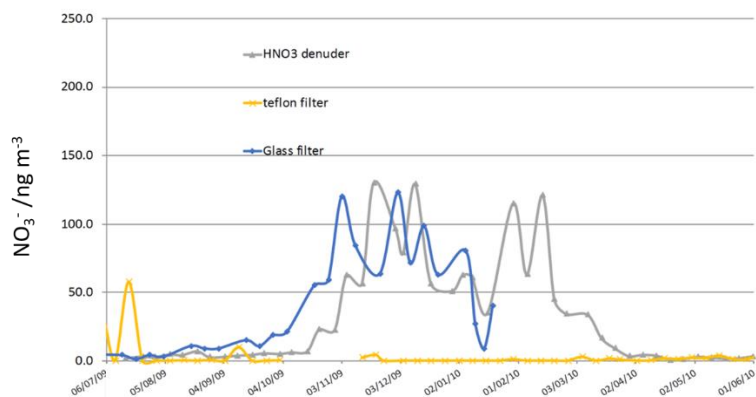
However, although we cannot cite any published study that proves the efficiency of  $\text{HNO}_3$  collection using GF filters, we would like to share here our own investigation into this topic which provides some support. Figure 1 below shows a comparison of nitrate concentrations obtained from collections 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  $\text{HNO}_3$  in summer, reaching around  $100 \text{ ng m}^{-3}$ , which is 10 times higher than the  $p\text{-NO}_3^-$  concentration (Legrand et al., 2017). As our nitrate concentrations also reach around  $100 \text{ ng m}^{-3}$  in summer, this means that we are necessarily effectively collecting  $\text{HNO}_3$ . 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  $100 \text{ ng m}^{-3}$  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  $\text{HNO}_3$  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  $\text{ng m}^{-3}$  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  $\text{NO}_3^-$  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  $\text{HNO}_3$  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  $\text{HNO}_3$  (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  $p\text{-NO}_3^-$ , we are confident that the high GF filter NaCl loading allowed the quantitative collection of  $\text{HNO}_3$  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  $\text{NO}_3^-$  between the gaseous phase ( $\text{HNO}_3$ ) and/or aerosols phase ( $p\text{-NO}_3^-$ ) during transport, the studies you cite were carried out in remote regions (Greenland and the Tibetan Plateau) and are based on  $\text{NO}_3^-$  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  $\text{NO}_3^-$  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  $\text{NO}_3^-$  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- $\text{NO}_3^-$  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<sub>x</sub> 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<sub>3</sub><sup>-</sup> 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<sub>3</sub> 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<sub>3</sub><sup>-</sup> collected at the surface. This influence of a change in NO<sub>3</sub><sup>-</sup> 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<sub>2</sub><sup>-</sup>)? 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<sup>15</sup>N and d<sup>18</sup>O of nitrate and trace metal chemistry, *Marine Chemistry*, [doi:10.1016/j.marchem.2009.01.013](https://doi.org/10.1016/j.marchem.2009.01.013).**

The integrity of the isotopic composition of NO<sub>2</sub><sup>-</sup> 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<sub>2</sub><sup>-</sup>. In short, matrix alkalinity limits O isotopic exchanges between NO<sub>2</sub><sup>-</sup> and water to some extent. For more details on our study of the stability of the NO<sub>2</sub><sup>-</sup> 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<sub>2</sub><sup>-</sup> 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 <sup>17</sup>O (unpublished data currently being analysed for intercomparison purposes).

The N and O isotopes of  $\text{NO}_2^-$  analytes are only scaled relative to the  $\text{NO}_2^-$  reference materials (see the detailed calibration procedure in Albertin et al., 2021). The isotopic composition of  $\text{NO}_3^-$  cannot be measured with the azide method because it does not convert  $\text{NO}_3^-$  to  $\text{N}_2\text{O}$ , but only to  $\text{NO}_2^-$ . We chose to carry out a calibration based on  $\text{NO}_2^-$  standards, assuming conservation of  $\Delta^{17}\text{O}$ . If  $\text{NO}_3^-$  were used, this would require a reduction step to  $\text{NO}_2^-$  on activated cadmium, a process that is difficult to reproduce under equivalent conditions and during which we cannot certify the conservation of  $\Delta^{17}\text{O}$ .

- 4) The crux of the interpretation and conclusion rely on  $\text{NO}_2$  having a short lifetime such that production of nitrate from  $\text{NO}_2$  is controlled by local chemistry. The lifetime of  $\text{NO}_2$  photolysis is calculated, but the lifetime of  $\text{NO}_2$  loss (as nitrate) is not. The calculation of  $\Delta^{17}\text{O}$ -nitrate relies on  $\Delta^{17}\text{O}(\text{NO}_2)$ . At each time step (3 h interval) the nitrate is calculated from the  $\text{NO}_2$ . A weighted average of the  $\Delta^{17}\text{O}\text{-NO}_3^-$  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  $\text{NO}_2$  to nitrate. The weighting of each 3 h interval for  $\text{NO}_3^-$  is based on  $[\text{NO}_2]^*J_{\text{NO}_2}$  as a proxy for OH production. These values also represent a time when  $\text{NO}_2$  is being photolyzed, not converted by OH to nitrate. When the nitrate  $\Delta^{17}\text{O}$  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  $\Delta^{17}\text{O}\text{-NO}_2$  is relevant to the  $\Delta^{17}\text{O}\text{-NO}_3^-$  collected. This all ends up a bit messy (albeit complex). It seems that it might make more sense to calculate an average (weighted) daytime  $\Delta^{17}\text{O}\text{-NO}_2$  and then calculate an average  $\Delta^{17}\text{O}\text{-NO}_3^-$  from this weighted  $\text{NO}_2$ . There is not a direct link between the simultaneously collected  $\text{NO}_2$  and  $\text{NO}_3^-$  - in other words, the  $\text{NO}_3^-$  collected in that time interval cannot be from the  $\text{NO}_2$  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  $\Delta^{17}\text{O}\text{-NO}_2$  to predict average  $\text{NO}_3^-$  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  $\text{NO}_2$  in to  $\text{HNO}_3$ . 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  $\Delta^{17}\text{O}(\text{NO}_2)$  between 7:30 and 18:00 LT, which are now compared with observed  $\Delta^{17}\text{O}(\text{NO}_3^-)$  averaged over the same period. At night, we average observed  $\Delta^{17}\text{O}(\text{NO}_2)$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  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  $\Delta^{17}\text{O}(\text{NO}_3^-)$  is still greater during SP 2 than during SP 1. We have also modified the average period for  $\delta^{15}(\text{NO}_2)$  and  $\delta^{15}(\text{NO}_3^-)$  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  $\text{NO}_3^-$ .

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

		$\Delta^{17}\text{O}(\text{NO}_2) / \text{‰}$	$\Delta^{17}\text{O}(\text{NO}_3^-) / \text{‰}$	$\Delta^{17}\text{O}_{\text{calc}}(\text{NO}_3^-) / \text{‰}$	$\Delta^{17}(\text{NO}_3^-_{\text{calc}} - \text{NO}_3^-_{\text{obs}})$
Daytime (7:30-18:00)	SP 1	$30.0 \pm 7.3$	$23.0 \pm 3.1$	$22.5 \pm 4.6$	-0.5
	SP 2	$26.1 \pm 6.9$	$23.9 \pm 3.8$	$17.5 \pm 4.6$	-6.4
Nighttime (18:00-7:30)	SP 1	$21.2 \pm 1.1$	$20.5 \pm 1.1$	$21.4 \pm 0.7$	0.9
	SP 2	$20.8 \pm 1.0$	$23.2 \pm 1.0$	$21.0 \pm 0.6$	-2.2

**Table 2.** Mean observed  $\Delta^{17}\text{O}$  data of  $\text{NO}_2$  ( $\Delta^{17}\text{O}(\text{NO}_2)$ ) and  $\text{NO}_3^-$  ( $\Delta^{17}\text{O}(\text{NO}_3^-)$ ) in Chamonix, and mean calculated  $\Delta^{17}\text{O}$  of  $\text{NO}_3^-$  ( $\Delta^{17}\text{O}_{\text{calc}}(\text{NO}_3^-)$ ) using Eqs. (6) and (7) at day and night, respectively, constrained with observed  $\Delta^{17}\text{O}(\text{NO}_2)$ . Day and night calculated values were weighted by  $[\text{NO}_2] \times J_{\text{NO}_2}$  and  $[\text{NO}_2] \times [\text{O}_3]$ , respectively

		$\delta^{15}\text{N}(\text{NO}_2) / \text{‰}$	$\delta^{15}\text{N}(\text{NO}_3^-) / \text{‰}$	$\delta^{15}\text{N}(\text{NO}_x) / \text{‰}$	$\delta^{15}\text{N}(\text{NO}_3^- - \text{NO}_2) / \text{‰}$
Daytime (7:30-18:00)	SP 1	$7.4 \pm 4.7$	$7.0 \pm 6.7$	$-9.9 \pm 2.9$	-0.4
	SP 2	$14.0 \pm 13.9$	$4.0 \pm 6.4$	$-10.8 \pm 2.1$	-10.0
Nighttime (18:00-7:30)	SP 1	$-5.1 \pm 2.3$	$1.4 \pm 1.2$	$-9.0 \pm 0.8$	6.3
	SP 2	$-2.5 \pm 4.2$	$-1.1 \pm 0.4$	$-9.9 \pm 1.9$	1.4

**Table 4.** Mean observed  $\delta^{15}\text{N}$  data of  $\text{NO}_2$  ( $\delta^{15}\text{N}(\text{NO}_2)$ ) and  $\text{NO}_3^-$  ( $\delta^{15}\text{N}(\text{NO}_3^-)$ ), calculated atmospheric  $\delta^{15}\text{N}$  of  $\text{NO}_x$  ( $\delta^{15}\text{N}(\text{NO}_x)$ , and  $\delta^{15}\text{N}$  shift between  $\delta^{15}\text{N}(\text{NO}_3^-)$  and  $\delta^{15}\text{N}(\text{NO}_2)$  ( $\Delta^{15}(\text{NO}_3^- - \text{NO}_2)$ ).

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  $\Delta^{17}\text{O}(\text{NO}_3^-)$  at our site, one compare observed  $\Delta^{17}\text{O}(\text{NO}_3^-)$  with estimated values of  $\Delta^{17}\text{O}(\text{NO}_3^-)$  derived from  $\Delta^{17}\text{O}$  mass balance and observed  $\Delta^{17}\text{O}(\text{NO}_2)$ , assuming the OH and  $\text{N}_2\text{O}_5$  pathways dominate the formation of  $\text{NO}_3^-$  at our site. Therefore, calculated  $\Delta^{17}\text{O}(\text{NO}_3^-)$  reflect the theoretical  $\Delta^{17}\text{O}$  transfer during the oxidation of  $\text{NO}_2$  to  $\text{NO}_3^-$  at our site through the dominant chemical process during the day (i.e. OH pathway) and at night (i.e.  $\text{N}_2\text{O}_5$  pathway).

As presented, during the day, we consider that the conversion of  $\text{NO}_2$  into  $\text{NO}_3^-$  is predominantly influenced by Reaction (R5) (OH pathway). Hence, the theoretical corresponding  $^{17}\text{O}$ -excess transfer to  $\text{NO}_3^-$  is estimated using Eq. (6) and observed  $\Delta^{17}\text{O}(\text{NO}_2)$  between 7:30 and 18:00 LT ( $n = 3$  per sampling period). Then, in order to estimate a daytime average value of  $\Delta^{17}\text{O}(\text{NO}_3^-)$  which is representative of the potential for the formation of  $\text{NO}_3^-$  from surface  $\text{NO}_2$  by the OH pathway, each calculated  $\Delta^{17}\text{O}(\text{NO}_3^-)$  is weighted by the product  $[\text{NO}_2] \times J_{\text{NO}_2}$  (the diurnal variability of the OH mixing ratio is assumed to follow the diurnal  $J_{\text{NO}_2}$  variation; Liu et al., 2021). Finally,



an overall mean daytime  $\Delta^{17}\text{O}(\text{NO}_3^-)$  for SP 1 and SP 2 is estimated by taking the sum of the weighted calculated values ( $=\Delta^{17}\text{O}_{\text{calc}}(\text{NO}_3^-)$ ). The same approach is used during the night, assuming that the conversion of  $\text{NO}_2$  into  $\text{NO}_3^-$  is dominated by Reactions (R6)–(R8) ( $\text{N}_2\text{O}_5$  pathway). Eq.(7) and observed  $\Delta^{17}\text{O}(\text{NO}_2)$  between 18:00 and 7:30 LT ( $n = 3$  per sampling day) are used to estimate  $\Delta^{17}\text{O}(\text{NO}_3^-)$ . Each calculated  $\Delta^{17}\text{O}(\text{NO}_3^-)$  is weighted by the product  $[\text{NO}_2] \times [\text{O}_3]$  (i.e.,  $\text{NO}_3^-$  production rate) and summed to estimate a mean nighttime  $\Delta^{17}\text{O}(\text{NO}_3^-)$  for SP 1 and SP 2. The  $^{17}\text{O}$ -excess transferred from  $\text{O}_3$  to  $\text{NO}_2$  during Reaction (R6) ( $\Delta^{17}\text{O}_{\text{NO}_2+\text{O}_3}(\text{NO}_3^-)$ ) is fixed at 44.7 ‰. This value is set accordingly to the transfer function reported by Berhanu et al. (2012) whereby  $\Delta^{17}\text{O}_{\text{NO}_2+\text{O}_3}(\text{NO}_3^-) = (1.23 \pm 0.19) \times \Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}} + (9.02 \pm 0.99)$  and  $\Delta^{17}\text{O}(\text{O}_3)_{\text{bulk}} = 29.0$  ‰ (see Section 2.4.1). We compare hereafter  $\Delta^{17}\text{O}_{\text{calc}}(\text{NO}_3^-)$  with the weighted day and night averages of observed  $\Delta^{17}\text{O}(\text{NO}_3^-)$  at our site. During the day,  $\Delta^{17}\text{O}_{\text{calc}}(\text{NO}_3^-)$  is compared with  $\Delta^{17}\text{O}(\text{NO}_3^-)$  observations averaged between 7:30 and 18:30 LT ( $n = 3$ ). At night,  $\Delta^{17}\text{O}_{\text{calc}}(\text{NO}_3^-)$  is compared with  $\Delta^{17}\text{O}(\text{NO}_3^-)$  observations averaged between 18:30 to 7:30 LT.

At night during SP 1, observed  $\Delta^{17}\text{O}(\text{NO}_3^-)$  and  $\Delta^{17}\text{O}_{\text{calc}}(\text{NO}_3^-)$  are in good agreement ( $\Delta^{17}\text{O}_{\text{calc}}(\text{NO}_3^-) - \Delta^{17}\text{O}(\text{NO}_3^-) = \Delta^{17}(\text{NO}_3^-_{\text{calc}} - \text{NO}_3^-_{\text{obs}}) = 0.9$  ‰), suggesting a local and rapid ( $< 12$  h) conversion of  $\text{NO}_2$  into  $\text{NO}_3^-$  via the  $\text{N}_2\text{O}_5$  pathway. During the day, observed  $\Delta^{17}\text{O}(\text{NO}_3^-)$  is 0.5 ‰ higher than  $\Delta^{17}\text{O}_{\text{calc}}(\text{NO}_3^-)$ , also suggesting that  $\text{NO}_3^-$  is formed locally during the day for oxidation of surface  $\text{NO}_2$  through the OH pathway. Small differences between observed and calculated  $\Delta^{17}\text{O}$  of  $\text{NO}_3^-$  during the day/night could be explained by the presence of  $\text{NO}_3^-$  residues formed during the previous night/day, which are not considered in the calculations since they do not account for  $\text{NO}_3^-$  lifetime. In contrast to SP 1,  $\Delta^{17}\text{O}_{\text{calc}}(\text{NO}_3^-)$  during SP 2 is significantly lower than the mean observed  $\Delta^{17}\text{O}(\text{NO}_3^-)$ , particularly during the day with a  $\Delta^{17}(\text{NO}_3^-_{\text{calc}} - \text{NO}_3^-_{\text{obs}})$  of  $-6.4$  ‰. The significant gap between observed and calculated  $\Delta^{17}\text{O}(\text{NO}_3^-)$  suggests a different origin and/or formation process of  $\text{NO}_3^-$  during SP 2 compared to SP 1. Although less important than during the day,  $\Delta^{17}\text{O}_{\text{calc}}(\text{NO}_3^-)$  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  $\text{NO}_3^-$ . It is important to point out that, although the  $\text{NO}_2$  sample collected on Feb 24 between 13:30 and 16:30 LT presents an important blank (ca. 14 ‰), ambient  $\text{NO}_2$  is low during the sampling period (mean of  $(4.5 \pm 1.8)$  nmol mol $^{-1}$ ). Therefore, as each  $\Delta^{17}\text{O}$  value used to estimate  $\Delta^{17}\text{O}_{\text{calc}}(\text{NO}_3^-)$  is weighted by the mean ambient  $\text{NO}_2$  mixing ratio over the sampling period, the uncertainty related to this blank has little influence on the daily average of  $\Delta^{17}\text{O}_{\text{calc}}(\text{NO}_3^-)$ . Given the low  $\Delta^{17}(\text{NO}_3^-_{\text{calc}} - \text{NO}_3^-_{\text{obs}})$  during SP 1, observed  $\Delta^{17}\text{O}(\text{NO}_3^-)$  can be explained by the local and rapid ( $< 12$  h) oxidation of  $\text{NO}_2$ , dominated by the OH and  $\text{N}_2\text{O}_5$  pathway during the day and night, respectively. However, in contrast to SP 1, the  $^{17}\text{O}$ -excess measured in  $\text{NO}_3^-$  during the day of SP 2 cannot be fully constrained by the oxidation of surface  $\text{NO}_2$  through the OH pathway, suggesting that the formation mechanisms of  $\text{NO}_3^-$  are different between SP 1 and SP 2 and/or the presence of  $\text{NO}_3^-$  not formed locally during SP 2. Below we examine the changes in the sub-daily dynamics of  $\Delta^{17}\text{O}(\text{NO}_3^-)$  between SP 1 and SP 2 in light of atmospheric observations.”

and as (lines 726-760):

“ $\delta^{15}\text{N}(\text{NO}_3^-)$  also exhibits substantial variability during the day, ranging from  $-1.3\text{‰}$  to  $14.9\text{‰}$  and from  $-4.2\text{‰}$  to  $9.7\text{‰}$  during SP 1 and SP 2, respectively. At night,  $\delta^{15}\text{N}(\text{NO}_3^-)$  is less variable, with an overall mean of  $(1.4 \pm 1.2)\text{‰}$  and  $(-1.1 \pm 0.4)\text{‰}$  during SP 1 and SP 2, respectively.  $\delta^{15}\text{N}(\text{NO}_3^-)$  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<sub>2</sub> 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 <sup>15</sup>N partitioning between NO<sub>x</sub> emissions and NO<sub>2</sub>, the latter being enriched in <sup>15</sup>N compared to NO<sub>x</sub> emissions. Interestingly, important enrichments in <sup>15</sup>N are also observed in NO<sub>3</sub><sup>-</sup>.

As described above, at night during SP 1 and SP 2,  $\delta^{15}\text{N}(\text{NO}_2)$  is close to  $\delta^{15}\text{N}(\text{NO}_x)$  due to small N fractionation effects. However, between 18:00–7:30 LT, NO<sub>3</sub><sup>-</sup> is enriched in <sup>15</sup>N relative to NO<sub>2</sub> by  $+6.3\text{‰}$  and  $+1.4\text{‰}$  in average during SP 1 and SP 2, respectively (Table 4). If we assume that, at night, NO<sub>3</sub><sup>-</sup> is formed mainly by the conversion of surface NO<sub>2</sub> via the N<sub>2</sub>O<sub>5</sub> pathway, then the difference between  $\delta^{15}\text{N}(\text{NO}_3^-)$  and  $\delta^{15}\text{N}(\text{NO}_2)$  ( $\Delta^{15}(\text{NO}_3^- - \text{NO}_2)$ ) should reflect the N enrichment factor associated to this oxidation process. It is likely that an isotopic equilibrium is established between NO<sub>2</sub>, NO<sub>3</sub>, and N<sub>2</sub>O<sub>5</sub>, hence affecting the partitioning of <sup>15</sup>N between NO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> produced at night (Walters and Michalski, 2016). Neglecting KIE associated with the N<sub>2</sub>O<sub>5</sub> pathway and using the expression of the EIE fractionation factor between N<sub>2</sub>O<sub>5</sub> and NO<sub>2</sub> given by Walters and Michalski (2015) (Appendix D) constrained with the mean nighttime temperature at our site, the isotopic composition of NO<sub>3</sub><sup>-</sup> is expected to be enriched in <sup>15</sup>N by about 29‰ compared to NO<sub>2</sub>. This estimated <sup>15</sup>N enrichment is about three times higher than the observed  $\Delta^{15}(\text{NO}_3^- - \text{NO}_2)$  at our site. As daytime NO<sub>3</sub><sup>-</sup> exhibits higher  $\delta^{15}\text{N}$  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<sub>2</sub> and NO<sub>3</sub><sup>-</sup>. These results highlight the importance of improving our understanding of the <sup>15</sup>N fractionation between NO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> associated with the N<sub>2</sub>O<sub>5</sub> pathway. This could be achieved in an atmospheric simulation chamber that allows to reproduce individual processes in controlled conditions. The <sup>15</sup>N isotopic enrichment of NO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> collected from 7:30 to 18:00 LT shows a very contrasted distribution between SP 1 and SP 2, with a respective average  $\Delta^{15}(\text{NO}_3^- - \text{NO}_2)$  of  $-0.4\text{‰}$  and  $-10.0\text{‰}$  (Table 4). Although subjected to significant uncertainties (Fan et al., 2019), the OH pathway is often associated to a KIE effect of  $-3\text{‰}$  (Freyer, 1991), which is at odds with our observations. Similarly to the N<sub>2</sub>O<sub>5</sub> pathway, there is an important need to better estimate the fractionation factor associated with the OH pathway.

There are significant differences in  $\Delta^{15}(\text{NO}_3^- - \text{NO}_2)$  between SP 1 and SP 2, providing further evidence that NO<sub>3</sub><sup>-</sup> collected during these two periods has undergone different formation processes and/or originate from different sources of NO<sub>2</sub>. In addition, possible fractionation associated with phase change between HNO<sub>3</sub> and *p*-NO<sub>3</sub> during transport of Saharan dust could influence the  $\delta^{15}\text{N}$  of collected NO<sub>3</sub><sup>-</sup> during SP 2. However, given the lack of knowledge about N fractionation factors between NO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> and our limited dataset, we cannot conclude whether the changes in the distribution of NO<sub>3</sub><sup>-</sup> isotopes during SP 2 result from changes in the phase distribution of NO<sub>3</sub><sup>-</sup> or in NO<sub>2</sub> oxidation processes.”

In hindsight, a key aspect to consider when comparing calculated and observed  $\Delta^{17}\text{O}(\text{NO}_3^-)$  is not actually the timescale for conversion of  $\text{NO}_2$  into  $\text{NO}_3^-$ , but rather the residence time of  $\text{NO}_3^-$ , which is determined by deposition. Indeed, if  $\text{NO}_3^-$  residence time was significantly shorter than the averaging period of  $\Delta^{17}\text{O}(\text{NO}_2)$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$ , most of the  $\text{NO}_3^-$  sampled during a specific averaging period would originate from  $\text{NO}_2$  oxidised during the same period. Reversely, if  $\text{NO}_3^-$  residence time was much longer than the averaging period, most of  $\text{NO}_3^-$  sampled during a specific averaging period would come from  $\text{NO}_2$  from previous averaging periods. Here,  $\text{NO}_3^-$  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  $\text{NO}_3^-$  is expected to reflect nocturnal oxidation of  $\text{NO}_2$ , especially towards the end of the night. During the day,  $\text{NO}_3^-$  is more likely to reflect both daily oxidation of  $\text{NO}_2$  and nocturnal  $\text{NO}_3^-$  because residues of nocturnal  $\text{NO}_3^-$  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  $\text{RO}_2$  radicals in wintertime. HONO, however, is not brought at all into the interpretation of the  $\delta^{15}\text{N}$ . Both the  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  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  $\text{NO}_x$  emissions from anthropogenic sources, it is unlikely that the production of NO by HONO photolysis would have a significant impact on the  $\delta^{15}\text{N}$  of  $\text{NO}_2$  and  $\text{NO}_3^-$ . 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  $\text{NO}_x$  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  $\text{h}^{-1}$  in Tai'an (Xue et al., 2022), 2.6 ppb  $\text{h}^{-1}$  in Beijing (Spataro et al., 2013), 0.7 ppb  $\text{h}^{-1}$  in Paris (Michoud et al., 2014), and 1.77 ppb  $\text{h}^{-1}$  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- $\text{NO}_2$  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  $\text{NO}_2$  drive the main variability of  $\delta^{15}\text{N}$  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 ( $\Delta^{17}\text{O}$ ) and nitrogen ( $\delta^{15}\text{N}$ ) isotopic compositions of atmospheric nitrate ( $\text{NO}_3^-$ ) are widely used as tracers of its formation pathways, precursor (nitrogen oxides ( $\text{NO}_x$ )  $\equiv$  nitric oxide (NO) + nitrogen dioxide ( $\text{NO}_2$ )) emission sources, and physico-chemical processing. However, the lack of observations on the multi-isotopic composition of  $\text{NO}_2$  maintains significant uncertainties regarding the quantitative links between the isotopic composition of  $\text{NO}_x$  and  $\text{NO}_3^-$ , which ultimately may bias inferences on  $\text{NO}_3^-$  formation processes and distribution of sources, particularly in winter urban atmospheres. We report here on the first simultaneous atmospheric observations of  $\Delta^{17}\text{O}$  and  $\delta^{15}\text{N}$  in  $\text{NO}_2$  ( $n = 16$ ) and  $\text{NO}_3^-$  ( $n = 14$ ). The measurements were carried out at sub-daily ( $\sim 3$  h) resolution over two non-consecutive days in an Alpine city in February 2021. A strong diurnal signal is observed in both  $\text{NO}_2$  and  $\text{NO}_3^-$  multi-isotopic composition.  $\Delta^{17}\text{O}$  of  $\text{NO}_2$  and  $\text{NO}_3^-$  ranges from 19.6 ‰ to 40.8 ‰ and from 18.3 ‰ to 28.1 ‰, respectively. During the day and night, the variability of  $\Delta^{17}\text{O}(\text{NO}_2)$  is mainly driven by the oxidation of NO by ozone, with a substantial contribution from peroxy radicals in the morning.  $\text{NO}_3^-$  mass balance equations, constrained by observed  $\Delta^{17}\text{O}(\text{NO}_2)$ , suggest that during the first day of sampling, most of  $\text{NO}_3^-$  was formed locally from the oxidation of  $\text{NO}_2$  by hydroxyl radicals by day, and via heterogeneous hydrolysis of dinitrogen pentoxide at night. For the second day, calculated and observed  $\Delta^{17}\text{O}(\text{NO}_3^-)$  do not match, particularly daytime values; the possible effects on  $\Delta^{17}\text{O}(\text{NO}_3^-)$  of a Saharan dust event that occurred during this sampling period and of winter boundary layer dynamics are discussed.  $\delta^{15}\text{N}$  of  $\text{NO}_2$  and  $\text{NO}_3^-$  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  $\delta^{15}\text{N}(\text{NO}_2)$  is explained by significant post-emission equilibrium N fractionation. After accounting for this effect, vehicle exhaust is found to be the primary source of  $\text{NO}_x$  emissions at the sampling site.  $\delta^{15}\text{N}(\text{NO}_3^-)$  is closely linked to  $\delta^{15}\text{N}(\text{NO}_2)$  variability, bringing further support to relatively fast and local  $\text{NO}_x$  processing. Uncertainties on current N fractionation factors during  $\text{NO}_2$  to  $\text{NO}_3^-$  conversion are underlined. Overall, this detailed investigation highlights the potential and necessity to use simultaneously  $\Delta^{17}\text{O}$  and  $\delta^{15}\text{N}$  in  $\text{NO}_2$  and  $\text{NO}_3^-$  in order to better constrain quantitative inferences on the sources and formation chemistry of  $\text{NO}_3^-$  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”**

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<sub>3</sub><sup>-</sup> 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<sub>3</sub>(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<sub>x</sub> ≡ nitrogen monoxide (NO) + nitrogen dioxide (NO<sub>2</sub>)) remain more than two orders of magnitude higher than before the Industrial Revolution (Hoesly et al., 2018). Atmospheric nitrate (NO<sub>3</sub><sup>-</sup> ≡ nitric acid (HNO<sub>3</sub>) + particulate nitrate (*p*-NO<sub>3</sub><sup>-</sup>)), is the main end-product of NO<sub>x</sub> 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<sub>3</sub><sup>-</sup> 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<sub>r</sub>) 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<sub>x</sub> 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<sub>3</sub><sup>-</sup> concentration in air to NO<sub>x</sub> 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<sub>x</sub> conversion efficiency and the NO<sub>3</sub><sup>-</sup> 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 remains difficult to assess the contribution of each parameter to the non-linear N<sub>r</sub> 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<sub>3</sub>) 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<sub>x</sub> chemistry (e.g., Prabhakar et al., 2017; Alexander et al., 2020). Notably, NO<sub>3</sub><sup>-</sup> formation is generally dominated by homogeneous OH oxidation and heterogeneous O<sub>3</sub> 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<sub>x</sub>, mainly emitted as NO, undergoes oxidation to form NO<sub>2</sub>. During the day, a rapid photochemical equilibrium is established between NO and NO<sub>2</sub>, known as the "photostationary state" (PSS; Leighton, 1961), via key interconversion reactions (Reactions R1–R3):



This cycle can be disturbed by peroxy radicals (RO<sub>2</sub> ≡ hydroperoxyl radical (HO<sub>2</sub>) + methyl peroxy radical (CH<sub>3</sub>O<sub>2</sub>)) via typically Reaction (R4):

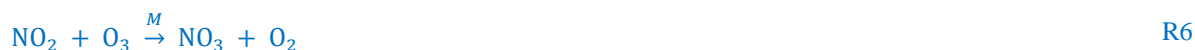


Note that in polluted atmospheres where NO<sub>x</sub> mixing ratios often exceed ppb levels, Reaction (R4) followed by Reactions (R1)–(R2) lead to the formation of O<sub>3</sub> (Crutzen, 1979). Although the role of RO<sub>2</sub> in NO<sub>x</sub> oxidation is crucial in O<sub>3</sub> formation and NO<sub>x</sub> oxidation rate, measuring RO<sub>2</sub> 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<sub>2</sub> in summer due to the high levels of O<sub>3</sub> and solar radiation, the shorter day length and lower temperature in winter result in a contrasted NO<sub>x</sub>

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<sub>3</sub> 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<sub>3</sub> 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<sub>x</sub> while VOCs emissions remain more or less constant (Ren et al., 2022). In urban areas, NO<sub>2</sub> is generally mainly removed from the atmosphere by reaction with OH during the day via Reaction (R5) (Dentener and Crutzen, 1993):



NO<sub>2</sub> can also react with O<sub>3</sub> to form nitrate radicals (NO<sub>3</sub>) via Reaction (R6):



However, NO<sub>3</sub> is rapidly photolyzed during the day regenerating back NO<sub>2</sub> (Wayne et al., 1991). Another important NO<sub>3</sub> 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<sub>3</sub> radicals substantially increases. NO<sub>3</sub> reacts with NO<sub>2</sub> to form dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>; Reaction R7), which then undergoes heterogeneous hydrolysis to form HNO<sub>3</sub> (Reaction R8):



Reaction (R7) is temperature dependent, so N<sub>2</sub>O<sub>5</sub> can eventually decompose to reform NO<sub>2</sub> and NO<sub>3</sub>, with the N<sub>2</sub>O<sub>5</sub>/NO<sub>3</sub> ratio being negatively correlated with temperature. N<sub>2</sub>O<sub>5</sub> is an important nocturnal sink for NO<sub>x</sub>, 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<sub>3</sub> can react with hydrocarbons to produce HNO<sub>3</sub>, which could significantly contribute to the formation of NO<sub>3</sub><sup>-</sup> 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<sub>3</sub><sup>-</sup> 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<sub>2</sub>O<sub>5</sub> pathway) are more contrasted and are still debated (e.g., Chan et al., 2021; Fu et al., 2020). In addition, the reaction of N<sub>2</sub>O<sub>5</sub> with chlorine on aerosols can contribute to NO<sub>3</sub><sup>-</sup> production in urban atmospheres (Thornton et al., 2010), with further impacts on O<sub>3</sub> 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<sub>3</sub><sup>-</sup> 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 ( $\delta$ ) 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  $\Delta^{17}O$  ( $26.2 \pm 1.3$ ) ‰; 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:

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

where  $\Delta^{17}O(NO_2)$  is the  $^{17}O$ -excess of atmospheric  $NO_2$  and  $\Delta^{17}O(\text{add. O})_i$  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-established 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  $\Delta^{17}\text{O}(\text{NO}_2)$  values and diel variability were consistent with its expected behaviour derived from  $\Delta^{17}\text{O}$  mass balance equations under the ISS assumption during the day. However, this first  $\Delta^{17}\text{O}(\text{NO}_2)$  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  $\Delta^{17}\text{O}(\text{NO}_2)$  measured by Albertin et al. (2021) is consistent with the oxidation of freshly emitted NO by  $\text{O}_3$ . Nonetheless, since the timescale for the oxidation of  $\text{NO}_2$  into  $\text{NO}_3^-$  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  $\text{NO}_2$  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  $\text{NO}_3^-$  chemistry may be more efficient. In such circumstances, the production of  $\text{NO}_3^-$  from  $\text{NO}_2$  formed at night would lead to a lower than expected  $\Delta^{17}\text{O}$  transfer to  $\text{NO}_3^-$ . For these reasons, the dual survey of the O isotopic composition of  $\text{NO}_2$  and  $\text{NO}_3^-$  would certainly help to accurately interpret  $\Delta^{17}\text{O}(\text{NO}_3^-)$  observations in polluted atmospheres, particularly with sampling at sub-daily time scales which would allow to study the diurnal dynamics of  $\Delta^{17}\text{O}(\text{NO}_2)$  and its links with  $\Delta^{17}\text{O}(\text{NO}_3^-)$ .

In addition to  $\Delta^{17}\text{O}$ ,  $\delta^{15}\text{N}$  in  $\text{NO}_3^-$  ( $\delta^{15}\text{N}(\text{NO}_3^-)$ ) can be used as a tracer of  $\text{NO}_3^-$  sources and/or chemical processing. As different  $\text{NO}_x$  emission sources have often distinct  $\delta^{15}\text{N}$ -fingerprints depending on the  $\text{NO}_x$  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),  $\delta^{15}\text{N}(\text{NO}_3^-)$  is a potentially valuable tool to trace the origins of its gaseous precursor. However, due to N fractionation effects associated with physico-chemical processing,  $\delta^{15}\text{N}$  is altered during the conversion of  $\text{NO}_x$  to  $\text{NO}_3^-$  (Elliott et al., 2019). Therefore, the variability of  $\delta^{15}\text{N}(\text{NO}_3^-)$  can be attributed to: (1) a change in  $\text{NO}_x$  emission sources and (2) N isotopic fractionations between NO and  $\text{NO}_2$ , between  $\text{NO}_2$  and  $\text{NO}_3^-$ , and during the transport of  $\text{NO}_3^-$ . These effects co-exist with relative contributions varying according to environmental conditions and the mix of  $\text{NO}_x$  emissions. Numerous observations in diverse environments have emphasised the substantial influence of N fractionation effects in altering the original  $^{15}\text{N}$  composition of emitted gaseous  $\text{NO}_3^-$  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  $\text{NO}_x$  and  $\text{NO}_3^-$ , which could lead to biased interpretations of  $\delta^{15}\text{N}(\text{NO}_3^-)$  observations.

Following the preliminary work of Albertin et al. (2021), this study presents for the first time the simultaneous measurements of the atmospheric  $\text{NO}_2$  and  $\text{NO}_3^-$  multi-isotopic compositions. The sampling took place at high temporal resolution ( $\sim 3$  h) in late February 2021 in an urban Alpine city.  $\Delta^{17}\text{O}/\delta^{15}\text{N}$  data of  $\text{NO}_2$  and  $\text{NO}_3^-$ , meteorological parameters, and atmospheric observations (NO,  $\text{NO}_2$ ,  $\text{O}_3$ , and PM) are collated in order to investigate diurnal N<sub>r</sub> chemistry, N fractionation effects and  $\text{NO}_x$  emissions. Our winter measurements extend the atmospheric  $\text{NO}_2$  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  $\text{NO}_2$ -based isotopic approaches for tracing the origins and fate of  $\text{NO}_x$ , for instance in urban areas on sub-daily time scales. The added value of  $\Delta^{17}\text{O}(\text{NO}_2)$  measurements in N<sub>r</sub> chemistry studies is more critically assessed here than in Albertin et al. (2021) through the use of accurate  $\text{NO}_x$  measurements. Besides, using the isotopic theoretical framework

developed previously, we explore the potential benefits of combining isotopic observations of  $\text{NO}_2$  and  $\text{NO}_3^-$  to gain a more detailed and quantitative on the links between atmospheric  $\text{N}_r$  chemistry processes and variability in  $\text{NO}_2$  and  $\text{NO}_3^-$  isotopic composition. The framework used in inferring dominant  $\text{NO}_x$  emission sources from  $\text{NO}_2$   $\delta^{15}\text{N}$  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  $\text{N}_2\text{O}_5$  can eventually decompose to reform  $\text{NO}_2$  and  $\text{NO}_3$ , with the  $\text{N}_2\text{O}_5/\text{NO}_3$  ratio being negatively correlated with temperature.”

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

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

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  $\text{NO}_x$  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  $\text{NO}_3^-$  between the gas and particle phase because our sampling method is design to collect both  $\text{HNO}_3$  and  $p\text{-NO}_3^-$  (see our response to your comment above) and it is the total nitrate that is the right metric to compare with  $\text{NO}_2$ .  $\text{HNO}_3$  and  $p\text{-NO}_3^-$  are in permanent exchange between these two phases, (e.g.,  $\text{H}_2\text{SO}_4 + p\text{-NO}_3^- \rightarrow p\text{-HSO}_4^- + \text{HNO}_3$  is a well-known acid displacement reaction) and it is even possible that  $^{15}\text{N}$  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  $\delta^{15}\text{N}(\text{NO}_3^-)$  during SP 2 in the presence of Saharan dust could reflect N fractionations related to a change of  $\text{NO}_3^-$  origin. This could be due to several reasons such as a change in  $\text{NO}_x$  precursors and/or in the contribution of  $\text{NO}_3^-$  formation pathways, especially if part of  $\text{NO}_3^-$  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  $\text{NO}_3^-$  in complex environments.

- **The “during transport of  $\text{NO}_3^-$  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  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  is determined by two main factors, namely the  $\delta^{15}\text{N}$ -fingerpring of the overall  $\text{NO}_x$  emission sources and the N fractionation effects that can alter the original  $\delta^{15}\text{N}(\text{NO}_x)$  value. However, for the sake of comprehensiveness, we prefer to maintain the mention of the N fractionation effect associated with  $\text{NO}_3^-$  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  $\delta^{15}\text{N}$  of atmospheric nitrate directly to performed  $\text{NO}_x$  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  $\text{NO}_x$  from this source, with very depleted isotopic ratios. Why is this snow-sourced  $\text{NO}_x$  not included in the discussion here?**

In winter in Chamonix, the snow-sourced  $\text{NO}_x$  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  $\text{NO}_x$  emissions far exceeds the potential flux from the snowpack. For these reasons, snow-sourced  $\text{NO}_x$  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  $\text{NO}$  and  $\text{NO}_2$  drive the main variability of  $\delta^{15}\text{N}$  at our site and that there is one dominant source of  $\text{NO}_x$  at our site from road traffic.

- **Lines 141-145: Evidence must be provided to support the assumption that total nitrate is collected ( $\text{HNO}_3$  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  $\text{HNO}_3$  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<sub>10</sub> 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<sup>3</sup> min<sup>-1</sup>)”

- **For the preservation of samples prior to isotopic analysis, how is it ensured that there is not exchange between the nitrite analyte (for NO<sub>2</sub>) 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 it 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<sub>3</sub><sup>-</sup> contribution from blank filters represented on average (8 ± 9) % of sampled NO<sub>3</sub><sup>-</sup>. Atmospheric mass concentrations (expressed in µg m<sup>-3</sup>) 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  $\text{NO}_3^-$  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  $\text{NO}_2$  samples did not allow for replicate measurements. From UV-vis analysis, all  $\text{NO}_2$  samples presented a negligible blank ( $< 4\%$ ; mean of  $1.7 \text{ nmol ml}^{-1}$ ) 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  $\Delta^{17}\text{O}$  of this sample was corrected for blank effect assuming that the contaminated  $\text{NO}_2^-$  possessed a  $\Delta^{17}\text{O} = 0\%$ . No correction from this blank effect was applied on the  $\delta^{15}\text{N}$  measurements of  $\text{NO}_2$  because the  $\delta^{15}\text{N}$  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  $\text{NO}_3^-$  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,  $\text{NO}_3^-$  reference materials ( $n = 4$ ) were prepared in different concentrations ( $n = 5$ ), from 40 nmol to 140 nmol.

As the azide method is specific to  $\text{NO}_2^-$  ions, possible  $\text{NO}_3^-$  contamination of denuder extractions does not impact the isotopic analysis of collected atmospheric  $\text{NO}_2$ .

- **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 NO<sub>2</sub> (as nitrite) and NO<sub>3</sub><sup>-</sup> (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<sub>3</sub><sup>-</sup> and NO<sub>2</sub> samples were evaluated using international NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> isotopic reference materials, respectively (Table S3 in the Supplement). Accuracy of the analytical method was estimated as the standard deviation ( $\sigma$ ) of the residuals between measurements of the reference materials and their expected values. In our study, average measurement uncertainties on  $\delta^{15}\text{N}$ ,  $\delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$ , and  $\Delta^{17}\text{O}$  were estimated to be  $\pm 0.3\text{‰}$ ,  $\pm 0.9\text{‰}$ ,  $\pm 1.3\text{‰}$ , and  $\pm 0.4\text{‰}$ , respectively, for NO<sub>3</sub><sup>-</sup> samples and  $\pm 0.3\text{‰}$ ,  $\pm 0.4\text{‰}$ ,  $\pm 0.9\text{‰}$ , and  $\pm 0.3\text{‰}$ , respectively, for NO<sub>2</sub> samples. Detailed information about the calibration procedure can be found in Morin et al. (2009) and in Albertin et al. (2021) for NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub> 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<sub>3</sub><sup>-</sup> samples, not NO<sub>2</sub>. 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  $\Delta^{17}\text{O}$  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<sub>2</sub> and NO<sub>3</sub><sup>-</sup> loss processes do not fractionate in terms of the oxygen mass-independent anomaly and considering that each source reaction induces a transfer of  $\Delta^{17}\text{O}$  to NO<sub>2</sub> and NO<sub>3</sub><sup>-</sup>, one consider the mass conservation of  $\Delta^{17}\text{O}$  during fractionation processes in the N<sub>r</sub> cycle. Hence, one can implement  $\Delta^{17}\text{O}$  in the general mass balance equation of NO<sub>2</sub> and NO<sub>3</sub><sup>-</sup>.”

- **Line 224: What is the lifetime for NO<sub>2</sub> 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<sub>2</sub> now, compared to NO<sub>3</sub><sup>-</sup> that was collected three hours later) needs to**

**be better justified. If the NO<sub>2</sub> lifetime is only minutes (Table B1) than the time frames should be the same for comparing NO<sub>2</sub> and NO<sub>3</sub><sup>-</sup>.**

**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 NO<sub>2</sub> has a 10 hour lifetime against loss (via deposition or chemistry). Therefore, the authors compare a single average nighttime measurement of NO<sub>2</sub> to NO<sub>3</sub><sup>-</sup>. In a closed system this would absolutely make sense. But in an open system, how can we ensure that the NO<sub>2</sub> collected during that time represents THE NO<sub>2</sub> that was converted to the sampled NO<sub>3</sub><sup>-</sup>? The authors make the assumption that this is true, then prove it by saying they can calculate the NO<sub>3</sub><sup>-</sup> based on the measured  $\Delta^{17}\text{O-NO}_2$  – this seems circular.**

If we consider an OH mixing ratio at ca.  $2 \times 10^6$  molec cm<sup>-3</sup> (average upper limit observed in different polluted environments at mid latitudes in winter; e.g., Tan et al., 2018; Stone et al., 2012) and  $k_{\text{NO}_2+\text{OH}} = 1.2 \times 10^{-11}$  cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup> (Atkinson et al., 2004), the lifetime for NO<sub>2</sub> during the day against chemical conversion into HNO<sub>3</sub> (i.e., OH oxidation) would be ca. 12 h. With regard to dry deposition, if we consider a NO<sub>2</sub> dry deposition velocity of 0.25 cm s<sup>-1</sup> (Holland et al., 1999) and a mean boundary layer height of 500 m, the lifetime for NO<sub>2</sub> during the day against dry deposition would be at an upper limit of ca. 56 h. Hence, NO<sub>2</sub> lifetimes against chemical loss and dry deposition are negligible in comparison with NO<sub>2</sub> photolysis which is about few minutes. However, what does really matter to compare <sup>17</sup>O-excess is NO<sub>3</sub><sup>-</sup> 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 NO<sub>3</sub><sup>-</sup> deposition velocity of 0.5 cm s<sup>-1</sup> (mean value of the dry deposition velocities of HNO<sub>3</sub> and *p*-NO<sub>3</sub><sup>-</sup>; 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 NO<sub>3</sub><sup>-</sup> 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 <sup>17</sup>O-excess in NO<sub>3</sub><sup>-</sup> 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 NO<sub>3</sub><sup>-</sup> against dry deposition are upper limits as they represent the time required to reduce by a factor *e* the concentration of NO<sub>3</sub><sup>-</sup> present at the top of the boundary layer; NO<sub>3</sub><sup>-</sup> 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  $\text{NO}_2$  present at the surface is that which is converted to  $\text{NO}_3^-$  (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  $\text{NO}_3^-$  does not originate solely from local oxidation of surface  $\text{NO}_2$ , 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  $\text{HNO}_3(\text{g})$  versus  $\text{NO}_3^-(\text{p})$  ignored in this section? It should clearly be stated why this is not included. While the collection of total  $\text{NO}_3^-$  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  $\text{HNO}_3(\text{g})$  versus  $\text{NO}_3^-(\text{p})$  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  $\text{HNO}_3(\text{g})$  and  $p\text{-NO}_3^-$  are collected (see our reply above). For clarity, we prefer to introduce gas-particle N fractionation effects only when we underline changes in the  $^{15}\text{N}$  distribution between SP 1 and SP 2 in Section 3.4.3.

- **Line 268: what is the “daytime  $\text{NO}_2$  chemistry lifetime” used here?**

As  $\text{NO}_2$  lifetime regarding OH oxidation is negligible in comparison to  $\text{NO}_2$  photolysis (see our response above), here the daytime  $\text{NO}_2$  chemistry lifetime refers to  $\text{NO}_2$  lifetime against photolysis, which is translated in the expression we give of  $A_{\text{day}}^*$ .

- **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:

## 1 Introduction

## 2 Material and methods

- 2.1 Study site and sample collection
- 2.2 Chemical and isotopic analysis
- 2.3 Ancillary data
- 2.4 Interpretation framework for isotopic signals
  - 2.4.1  $\Delta^{17}\text{O}$  mass balance equations
  - 2.4.2 Nitrogen isotopic fractionation effects

## 3 Results and Discussion

- 3.1 Temporal variations of general atmospheric observations
- 3.2  $\Delta^{17}\text{O}$  of  $\text{NO}_2$  and  $\text{NO}_x$  diurnal cycling
- 3.3 Interpretation of  $\Delta^{17}\text{O}$  in atmospheric nitrate
  - 3.3.1 Steady state evaluation of  $\Delta^{17}(\text{NO}_3^-)$
  - 3.3.2  $\Delta^{17}(\text{NO}_3^-)$  sub-daily dynamics
- 3.4 Nitrogen isotopic compositions
  - 3.4.1 N fractionation effects in the  $\text{NO}_x$  cycle
  - 3.4.2  $\text{NO}_x$  emission sources derived from  $\delta^{15}\text{N}(\text{NO}_2)$
  - 3.4.3 Interpretation of  $\delta^{15}\text{N}(\text{NO}_3^-)$  observations

## 4 Summary and implications

- **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  $\text{NO}_x$  chemistry. Most of the section 3.1 is really discussion of the results, not results. This should be amended. Is it a hypothesis that  $\text{O}_3$  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).

$\text{O}_3$  titration at 16:00 LT is supported by atmospheric observations (Figure 1) showing that  $\text{O}_3$  rapidly drops at that time following the rapid increase of  $\text{NO}_x$  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 7<sup>th</sup> and looks like a short term “event”. The time

**noted on the 23<sup>rd</sup> 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<sub>3</sub><sup>-</sup> 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<sub>3</sub><sup>-</sup> collected during SP 2. Indeed, Saharan dust can promote both the formation of NO<sub>3</sub><sup>-</sup> by heterogeneous hydrolysis and the condensation of HNO<sub>3</sub> already present in the atmosphere. The only statement we can make is that the change of O and N isotopic distribution of NO<sub>3</sub><sup>-</sup> 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<sub>3</sub><sup>-</sup> 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<sub>3</sub><sup>-</sup> 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<sub>3</sub><sup>-</sup> on day/night basis as (lines 497-516):

“Over the two sampling periods,  $\Delta^{17}\text{O}(\text{NO}_3^-)$  varies significantly (from 18.3 ‰ to 28.1 ‰), with a weighted mean of  $(22.5 \pm 3.1)$  ‰. While  $\Delta^{17}\text{O}(\text{NO}_2)$  values are relatively similar during the two sampling periods,  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values are systematically higher during SP 2 than during SP 1, except during the 7:30–10:00 LT interval.  $\Delta^{17}\text{O}(\text{NO}_3^-)$  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  $\Delta^{17}\text{O}(\text{NO}_2)$ , daytime and nighttime  $\Delta^{17}\text{O}(\text{NO}_3^-)$  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  $\Delta^{17}\text{O}(\text{NO}_3^-)$  and suggest that each sample reflects  $\text{NO}_3^-$  produced during both the day and night. From high-time-resolved (3 h) aerosol sampling in winter Beijing, Zhang et al. (2022b) reported  $\Delta^{17}\text{O}(\text{NO}_3^-)$  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  $\Delta^{17}\text{O}(\text{NO}_3^-)$  was attributed to the changes in the branching ratio of nocturnal and photochemical reactions on  $\text{NO}_3^-$  formation. In Chamonix, the range of  $\Delta^{17}\text{O}(\text{NO}_3^-)$  values are very different from Zhang et al. (2022) observations, with consistently lower values and a distinct diurnal tendency. However, in the cases of  $\Delta^{17}\text{O}(\text{NO}_3^-)$  measurements at sub-daily temporal scale, the atmospheric lifetime of  $\text{NO}_x$  and  $\text{NO}_3^-$  is critical for comparing  $\Delta^{17}\text{O}(\text{NO}_3^-)$  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  $\text{NO}_3^-$  mass concentration exceeding  $70 \mu\text{g m}^{-3}$ , 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  $\mu\text{g m}^{-3}$  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,  $\Delta^{17}\text{O}$  have been measured separately for  $\text{HNO}_3$  and  $p\text{-NO}_3^-$  in Kim et al. (2023), whereas we collected both  $\text{HNO}_3$  and  $p\text{-NO}_3^-$ . 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  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}$  of  $\text{NO}_2$  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

$\delta^{15}\text{N}(\text{NO}_2)$  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,  $\delta^{15}\text{N}(\text{NO}_2)$  shows substantial diurnal variability (from  $-10.0$  ‰ to  $19.7$  ‰,  $n = 16$ ) with a weighted mean of  $(4.0 \pm 9.1)$  ‰. In contrast, Albertin et al. (2021) reported a weak diurnal fluctuation of  $\delta^{15}\text{N}(\text{NO}_2)$  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  $\delta^{15}\text{N}(\text{NO}_2)$  values, however, unlike our study, these are almost consistently negative (from  $-31.4$  ‰ to  $0.4$  ‰) with an overall mean at  $(-11.4 \pm 6.9)$  ‰. As shown in Eq.(8), fluctuations in  $\delta^{15}\text{N}(\text{NO}_2)$  reflect changes in  $\text{NO}_x$  emission sources and/or N fractionation effects, these latter being weighted by  $1 - f_{\text{NO}_2}$  i.e., the more  $\text{NO}_x$  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  $f_{\text{NO}_2}$  ( $> 0.7$ ), isotope effects were small ( $< 2.7$  ‰) and  $\delta^{15}\text{N}(\text{NO}_2)$  was mostly driven by changing contribution of  $\text{NO}_x$  emission sources. At our site,  $f_{\text{NO}_2}$  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  $\delta^{15}\text{N}(\text{NO}_2)$ , respectively. This pronounced seasonal behaviour of N isotope fractionation effects within the  $\text{NO}_x$  cycle has previously been outlined in the seminal study of Freyer et al. (1993). Overall, compared with summer, lower  $f_{\text{NO}_2}$  during winter months due to lower  $\text{O}_3$  concentrations and higher  $\text{NO}_x$  emissions favour EIE between NO and  $\text{NO}_2$ , which also has a higher fractionation factor due to the lower temperatures (see Appendix B). Besides, this seasonal fluctuation of  $f_{\text{NO}_2}$  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  $\text{NO}_2$  at night due to a lower  $\text{NO}_x$  emission rate resulting in higher  $f_{\text{NO}_2}$  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)  $\text{RO}_2$  is defined as  $\text{RO}_2 = \text{HO}_2 + \text{CH}_3\text{O}_2$ . Equation 4 thus does not include reaction with  $\text{HO}_2$  separately. But this line makes it appear as if  $\text{RO}_2$  is being calculated from  $\text{HO}_2$  alone. Please clarify.**
- **Line 421: The calculated  $\text{RO}_2$  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  $\text{RO}_2$  estimates using  $\Delta^{17}\text{O}(\text{NO}_2)$  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  $\Delta^{17}\text{O}(\text{NO}_2)$  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  $\text{RO}_2$  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,  $\Delta^{17}\text{O}(\text{NO}_2)$  shows a large diurnal variability (from 19.6 ‰ to 40.8 ‰) with a weighted mean  $\pm$  one standard deviation of  $(25.2 \pm 7.1)$  ‰.  $\Delta^{17}\text{O}(\text{NO}_2)$  values during the day (7:30–18:00 LT,  $(28.5 \pm 7.3)$  ‰) are significantly higher ( $p$ -value = 0.002,  $n = 16$ ) than during the night (18:00–7:30 LT,  $(20.8 \pm 1.0)$  ‰). By day,  $\Delta^{17}\text{O}(\text{NO}_2)$  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,  $\Delta^{17}\text{O}(\text{NO}_2)$  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  $\Delta^{17}\text{O}(\text{NO}_2)$  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  $\Delta^{17}\text{O}(\text{NO}_2)$  reflects changes in the relative contributions of Reaction (R3) ( $\text{NO} + \text{O}_3$ ) and Reaction (R4) ( $\text{NO} + \text{RO}_2$ ) to the overall production of  $\text{NO}_2$ . At our site,  $\Delta^{17}\text{O}(\text{NO}_2)$  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  $\text{NO}_x$ - $\text{O}_3$  system is driven at first order by  $J_{\text{NO}_2}$  (Michalski et al., 2014), due to low solar radiation between 16:30–18:00 LT at our site, such a rapid drop of  $\Delta^{17}\text{O}(\text{NO}_2)$  suggests that sampled  $\text{NO}_2$  might not be at ISS anymore when the  $\text{NO}_2$  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  $\Delta^{17}\text{O}(\text{NO}_2)$  in the early evening reflects the rapid replacement of  $\text{NO}_2$  formed during the day by  $\text{NO}_2$  produced during the night via the conversion of freshly emitted  $\text{NO}$ , in line with Eq.(5). Then, high  $\text{NO}_2$  throughout the night, along with relatively low  $\text{O}_3$ , supports observations of low  $\Delta^{17}\text{O}(\text{NO}_2)$  at night (i.e.,  $\approx 20$  ‰).

Using Eq. (3**Erreur ! Source du renvoi introuvable.**), we derive from  $\Delta^{17}\text{O}(\text{NO}_2)$  observations the relative contribution of Reaction (R3) ( $\text{NO} + \text{O}_3$ ) to Reaction (R4) ( $\text{NO} + \text{RO}_2$ ) in the formation of  $\text{NO}_2$  ( $T_{\text{NO}+\text{O}_3}$ ):

$$T_{\text{NO}+\text{O}_3} = \frac{\Delta^{17}\text{O}_{\text{day}}(\text{NO}_2)}{\Delta^{17}\text{O}_{\text{NO}+\text{O}_3}(\text{NO}_2)} \quad (12)$$

Between 7:30 and 16:30 LT,  $T_{\text{NO}+\text{O}_3}$  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  $\text{NO} + \text{O}_3$  pathway is dominant between 13:30 and 16:30 LT, corresponding to the time when  $\text{O}_3$  is highest (Figure 1). In contrast, the maximum contribution for the  $\text{NO} + \text{RO}_2$  pathway is observed between 7:30 and 10:30 LT, when  $\text{NO}$  levels are high and rising continuously. Interestingly, previous studies reported a high sensitivity of  $\text{RO}_2$  to changes in  $\text{NO}_x$ , particularly at high  $\text{NO}_x$  levels (Ren et al., 2006; Stone et al., 2012). Sources of  $\text{RO}_2$  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  $\text{NO}_x/\text{O}_3/\text{RO}_2$  chemistry, particularly in the morning, as its photolysis can potentially accelerate daytime oxidation processes, leading to increased  $\text{RO}_2$  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  $\text{RO}_2$  mixing ratio from observed  $\Delta^{17}\text{O}(\text{NO}_2)$  and  $\text{O}_3$  mixing ratio following:

$$[\text{RO}_2] = \frac{k_{\text{NO}+\text{O}_3}[\text{O}_3]}{k_{\text{NO}+\text{RO}_2}} \left( \frac{\Delta^{17}\text{O}_{\text{NO}+\text{O}_3}(\text{NO}_2)}{\Delta^{17}\text{O}_{\text{day}}(\text{NO}_2)} - 1 \right) \quad (13)$$

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

and the updated Table 1:

Sampling interval (start - end)	$T_{\text{NO}+\text{O}_3}$	$\text{RO}_2/\text{pmol mol}^{-1}$
SP 1		
20/02 07:30 - 20/02 10:30	$0.72 \pm 0.01$	$0.86 \pm 0.75$
20/02 10:30 - 20/02 13:30	$0.91 \pm 0.01$	$1.77 \pm 0.36$
20/02 13:30 - 20/02 16:30	$1.00 \pm 0.01$	$0.00 \pm 0.91$
<i>Mean</i>	<i>0.88</i>	<i>0.88</i>
<i>Std dev.</i>	<i>0.14</i>	<i>0.88</i>
SP 2		
24/02 07:30 - 24/02 10:30	$0.55 \pm 0.01$	$0.58 \pm 1.67$
24/02 10:30 - 24/02 13:30	$0.86 \pm 0.01$	$3.56 \pm 0.50$
24/02 13:30 - 24/02 16:30	$0.84 \pm 0.08$	$10.63 \pm 6.75$
<i>Mean</i>	<i>0.75</i>	<i>4.92</i>
<i>Std dev.</i>	<i>0.18</i>	<i>5.16</i>

**Table 1.**  $T_{\text{NO}+\text{O}_3}$  and  $\text{RO}_2$  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  $\text{NO}_2$  sample collected on Feb 24 between 13:30 and 16:30 LT presents an important blank (ca. 14 %), ambient  $\text{NO}_2$  is low during the sampling period (mean of  $(4.5 \pm 1.8)$  nmol  $\text{mol}^{-1}$ ). Therefore, as each  $\Delta^{17}\text{O}$  value used to estimate  $\Delta^{17}\text{O}_{\text{calc}}(\text{NO}_3^-)$  is weighted by the mean ambient  $\text{NO}_2$  mixing ratio over the sampling period, the uncertainty related to this blank has little influence on the daily average of  $\Delta^{17}\text{O}_{\text{calc}}(\text{NO}_3^-)$ .”

- **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  $\text{N}_2\text{O}_5$ . But also note that not all reactions are included in the case study here – for instance  $\text{NO}_2$  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  $\Delta^{17}\text{O}$ , 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  $\Delta^{17}(\text{NO}_3^-_{\text{calc}} - \text{NO}_3^-_{\text{obs}})$  during SP 1, observed  $\Delta^{17}\text{O}(\text{NO}_3^-)$  can be explained by the local and rapid (< 12 h) oxidation of  $\text{NO}_2$ , dominated by the OH and  $\text{N}_2\text{O}_5$  pathway during the day and night, respectively. However, in contrast to SP 1, the  $^{17}\text{O}$ -excess measured in  $\text{NO}_3^-$  during the day of SP 2 cannot be fully constrained by the oxidation of surface  $\text{NO}_2$  through the OH pathway, suggesting that the formation mechanisms of  $\text{NO}_3^-$  are different between SP 1 and SP 2 and/or the presence of  $\text{NO}_3^-$  not formed locally during SP 2. Below we examine the changes in the sub-daily dynamics of  $\Delta^{17}\text{O}(\text{NO}_3^-)$  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  $\Delta^{17}\text{O}$  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  $\text{NO}_3^-$ .

- **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  $\text{NO}_3^-$  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  $\delta^{57}\text{N}$ . Furthermore, vehicle emissions could also be adding HONO, given that they are concluded as the primary source of local  $\text{NO}_x$  and  $\text{NO}_3^-$ . These pathways are neglected in the chemistry calculations and HONO impact on the  $\delta^{57}\text{N}$  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  $\delta^{57}\text{N}$  of NO produced from HONO photolysis, therefore, we cannot state that it would be very different from dominant  $\text{NO}_x$  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  $F_N$  ( $(43.6 \pm 3.3) \%$ ; 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  $\alpha_{\text{EIE}(\text{NO}_2/\text{NO})}$  used therein, to accurately describe the N fractionation between  $\text{NO}_x$  emissions and  $\text{NO}_2$  at our site, and hence, to describe most of the variability of  $\delta^{15}\text{N}(\text{NO}_2)$  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  $\delta^{15}\text{N}(\text{NO}_2)$  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.**

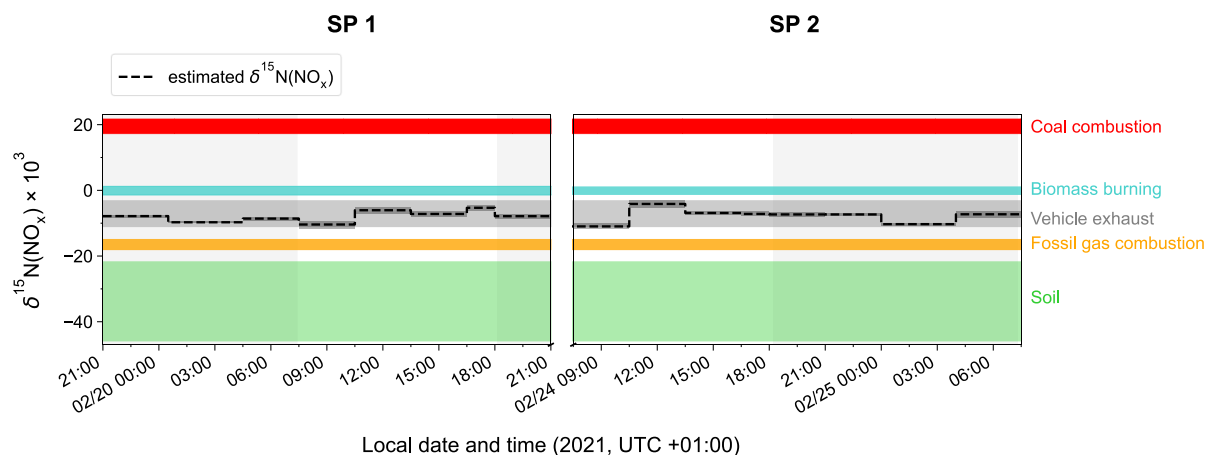
Thank you for pointing this out, it is a common issue in our research community. We acknowledge that the selected value may not be the most accurate to represent our sampling site. Nonetheless, it is difficult to determine the most appropriate value given the specific characteristics of our sampling site. Chamonix is located in a deep valley encompassed by high altitude mountains. As a result, emissions of  $\text{NO}_x$  at the surface are confined, particularly in winter. Hence, it is likely that ambient  $\text{NO}_x$  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-mountainous 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  $\text{NO}_x$  emissions in the morning when individuals leave their homes for work. Subsequently, during the day, we concur that  $\text{NO}_x$  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  $\delta^{15}\text{N}(\text{NO}_x)$  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  $\delta^{15}\text{N}(\text{NO}_x)$  derived from corrected  $\delta^{15}\text{N}(\text{NO}_2)$  is similar to that of Zong et al. (2017). Besides, we observe a slight increase of  $\delta^{15}\text{N}(\text{NO}_x)$  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  $\text{NO}_x$  from traffic emissions of the two main roads situated a few hundred meters away. In contrast, the lower  $\delta^{15}\text{N}(\text{NO}_x)$  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  $\delta^{15}\text{N}(\text{NO}_x)$  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  $\delta^{15}\text{N}(\text{NO}_x)$  for traffic. Song et al. (2022) obtained a very similar result to Zong et al. (2017) with a value of  $(-7.1 \pm 4.1)$ . 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  $\delta^{15}\text{N}(\text{NO}_x)$ . The revised manuscript includes this value as (lines 694-699):

“Regarding road traffic emissions, we have to stress that  $\delta^{15}\text{N}$  values reported in the literature are rather variable mainly because N fractionations during the process of  $\text{NO}_x$  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  $\delta^{15}\text{N}(\text{NO}_x)$  value given by Song et al. (2022) at  $(-7.1 \pm 4.1)$  ‰, calculated from 181 measurements reported in the literature.”

and Figure 4 has been updated accordingly:



**Figure 4.** Time evolution of  $\delta^{15}\text{N}(\text{NO}_x)$  (black dashed line) estimated from  $\delta^{15}\text{N}(\text{NO}_2)$  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  $\delta^{15}\text{N}$  value of individual  $\text{NO}_x$  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  $\text{NO}_x$  source.

In your comment, you underline that cold starts are brief, yet they emit the most  $\text{NO}_x$ , which means that we ought to detect the highest levels of  $\text{NO}$  in the morning rather than in the late afternoon. This is confirmed by Figure 1 of the manuscript showing much higher  $\text{NO}$  mixing ratios in the morning. However, we also acknowledge that the large uncertainty on the heating oil  $\delta^{15}\text{N}(\text{NO}_x)$  precludes a definite conclusion on our estimated  $\delta^{15}\text{N}(\text{NO}_x)$  reflecting only traffic emissions. It is possible that heating oil emissions play a role. However,  $\delta^{15}\text{N}(\text{NO}_x)$  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  $\text{NO}_x$  emission during its combustion can be classified as "Thermal- $\text{NO}_x$ " (in contrast with "Fuel- $\text{NO}_x$ "; Miller and Bowman, 1989). Thermal  $\text{NO}_x$  is generally depleted in  $^{15}\text{N}$  owing to kinetic fractionation effects when the  $\text{N}_2$  triple bond is broken, favouring the dissociation of the lightest isotopologue (Walters et al., 2015b). The mechanisms by which  $\text{NO}_x$  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  $\delta^{15}\text{N}$  footprint of  $\text{NO}_x$  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  $\delta^{15}\text{N}(\text{NO}_x)$  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<sub>x</sub> 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  $\delta^{15}\text{N}$  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<sub>x</sub> 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<sub>x</sub> removes NO<sub>x</sub> 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<sub>2</sub> to NO<sub>3</sub><sup>-</sup> 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<sub>3</sub><sup>-</sup> 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  $\Delta^{17}\text{O}$  mass balance equations of NO<sub>3</sub><sup>-</sup> constrained by observed  $\Delta^{17}\text{O}(\text{NO}_2)$  to assess whether NO<sub>3</sub><sup>-</sup> could originate locally from the oxidation of NO<sub>2</sub> at our site. During the first day of sampling,  $\Delta^{17}\text{O}$  records of NO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> support the local oxidation of NO<sub>2</sub> to NO<sub>3</sub><sup>-</sup> by OH radicals during the day, and via the heterogeneous hydrolysis of N<sub>2</sub>O<sub>5</sub> during the night. The second day of sampling was affected by a Saharan dust event,

accompanied by notable changes in the isotopic composition of  $\text{NO}_3^-$ . We propose that the formation of a surface inversion layer at night could have influenced the vertical distribution of  $\Delta^{17}\text{O}(\text{NO}_2)$  and resulted in a positive gradient of  $\Delta^{17}\text{O}(\text{NO}_3^-)$  with altitude, independently of the local  $\text{NO}_2$  to  $\text{NO}_3^-$  conversion processes near the surface. In such scenario, the presence of Saharan dust could have promoted heterogeneous  $\text{NO}_2$  oxidation leading to higher  $\Delta^{17}\text{O}$  in  $\text{NO}_3^-$  formed aloft. The latter would have then mixed with the  $\text{NO}_3^-$  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  $\Delta^{17}\text{O}$  in  $\text{NO}_3^-$  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  $\text{NO}_2$  and  $\text{NO}_3^-$  isotopic composition should be documented in order to explore the possible role of the boundary layer dynamics in the variability of  $\text{NO}_2$  and  $\text{NO}_3^-$  isotopic composition observed at the surface.”

## Technical comments:

- **Line 33: add () around NO and  $\text{NO}_2$ , i.e. (NO) ... ( $\text{NO}_2$ ) 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  $\text{HO}_2$  and  $\text{CH}_3\text{O}_2$ . For example, “This cycle can be disturbed by peroxy radicals (via R4;  $\text{RO}_2$  = hydroperoxyl radical ( $\text{HO}_2$ ) + methyl peroxy radical ( $\text{CH}_3\text{O}_2$ )) leading to formation of  $\text{O}_3$  (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<sub>2</sub> as well. i.e. make it clear that for the nighttime nitrate the NO<sub>2</sub> 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  $\Delta^{17}\text{O-NO}_2$  at night rather than  $\Delta^{17}\text{O-O}_3$ ? The only production channel at night is assumed to be  $\text{NO}+\text{O}_3$ , with presumably 1 oxygen from ozone and 1 from NO. Is it just implicit that  $\Delta^{17}\text{O-NO}_2$  formed at night =  $\Delta^{17}\text{O-O}_3$ ? This seems weird to not make this explicitly clear.**

Equation 5 uses  $\Delta^{17}\text{O}_{\text{night}}(\text{NO}_2)$  and not  $\Delta^{17}\text{O}(\text{O}_3)$  because it includes the residues of  $\Delta^{17}\text{O}_{\text{day}}(\text{NO}_2)$ .  $\Delta^{17}\text{O}_{\text{night}}(\text{NO}_2)$  would be equal to  $\Delta^{17}\text{O}(\text{O}_3)$  only when  $x$ , the fraction of  $\text{NO}_2$  formed during the day to the total  $\text{NO}_2$  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  $\text{NO}_x$  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  $\text{NO}_x$  in the form of  $\text{NO}_2$ ” 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  $\delta^{15}\text{N}(\text{NO}_2)$  can be derived as a function of a factor  $F_N$  which represents the overall N isotopic fractionation effects between  $\text{NO}_x$  emissions and  $\text{NO}_2$  (expressed in ‰), the fraction of  $\text{NO}_2$  with respect to  $\text{NO}_x$  ( $f_{\text{NO}_2} = [\text{NO}_2]/[\text{NO}_x]$ ), and of  $\delta^{15}\text{N}(\text{NO}_x)$  (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  $\text{NO}_x$  to  $\text{NO}_3^-$  conversion processes considered in this study, along with corresponding  $\Delta^{17}\text{O}$  transfer factors and the known  $^{15}\text{N}$  enrichment factors at 298 K (determined from both experimental and computational studies) are illustrated in Figure C1.”

- **Line 275:  $[\text{NO}_2]$  in the denominator should be  $[\text{NO}]$ , correct?**

$[\text{NO}_2]$  being at the denominator is correct as  $(1/k_{\text{NO}+\text{NO}_2}[\text{NO}_2])$  is the NO lifetime with respect to isotopic exchange with  $\text{NO}_2$ .



- **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 –  $\Delta^{17}\text{O}-\text{NO}_2$  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,  $\Delta^{17}\text{O}(\text{NO}_2)$  shows a large diurnal variability (from 19.6 ‰ to 40.8 ‰) with a weighted mean  $\pm$  one standard deviation of  $(25.2 \pm 7.1)$  ‰.  $\Delta^{17}\text{O}(\text{NO}_2)$  values during the day (7:30–18:00 LT,  $(28.5 \pm 7.3)$  ‰) are significantly higher ( $p$ -value = 0.002,  $n = 16$ ) than during the night (18:00–7:30 LT,  $(20.8 \pm 1.0)$  ‰). By day,  $\Delta^{17}\text{O}(\text{NO}_2)$  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,  $\Delta^{17}\text{O}(\text{NO}_2)$  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  $\Delta^{17}\text{O}(\text{NO}_2)$  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  $\Delta^{17}\text{O}(\text{NO}_2)$  reflects changes in the relative contributions of Reaction (R3) ( $\text{NO} + \text{O}_3$ ) and Reaction (R4) ( $\text{NO} + \text{RO}_2$ ) to the overall production of  $\text{NO}_2$ . At our site,  $\Delta^{17}\text{O}(\text{NO}_2)$  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  $\text{NO}_x-\text{O}_3$  system is driven at first order by  $J_{\text{NO}_2}$  (Michalski et al., 2014), due to low solar radiation between 16:30–18:00 LT at our site, such a rapid drop of  $\Delta^{17}\text{O}(\text{NO}_2)$  suggests that sampled  $\text{NO}_2$  might not be at ISS anymore when the  $\text{NO}_2$  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  $\Delta^{17}\text{O}(\text{NO}_2)$  in the early evening reflects the rapid replacement of  $\text{NO}_2$  formed during the day by  $\text{NO}_2$  produced during the night via the conversion of freshly emitted  $\text{NO}$ , in line with Eq. (5). Then, high  $\text{NO}_2$  throughout the night, along with relatively low  $\text{O}_3$ , supports observations of low  $\Delta^{17}\text{O}(\text{NO}_2)$  at night (i.e.,  $\approx 20$  ‰).”

- **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  $\Delta^{17}\text{O}$  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  $\text{O}_3$  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<sub>2</sub>...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<sub>2</sub> concentrations. This IS the time of the lowest T<sub>NO+O<sub>3</sub></sub> which means that the relative contribution of RO<sub>2</sub> 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 Δ<sup>17</sup>O to RO<sub>2</sub> concentration – i.e. calculated Δ<sup>17</sup>O values are not directly compared with the calculated RO<sub>2</sub> 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<sub>2</sub> 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:** Δ<sup>17</sup>O-NO<sub>2</sub> should be Δ<sup>17</sup>O-NO<sub>3</sub> here (with the subscript NO<sub>2</sub>+O<sub>3</sub>)

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<sub>r</sub> species, down to sub-daily temporal scales.”

- **Line 471:** the formatting for the Δ<sup>17</sup>O changes here

Indeed, this is because this Δ symbolises a difference between the two same quantities, Δ<sup>17</sup>O(NO<sub>3</sub><sup>-</sup><sub>calc</sub>) and Δ<sup>17</sup>O(NO<sub>3</sub><sup>-</sup><sub>obs</sub>), while Δ symbolises the deviation of δ<sup>17</sup>O to a reference value (0.52 × δ<sup>17</sup>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  $\Delta^{17}\text{O}(\text{NO}_3^-)$  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  $\delta^{15}\text{N}$  biomass exist and thus so should latitudinal difference in  $\delta^{15}\text{N}$ -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  $\delta^{15}\text{N}$  of traffic emission, choosing a  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}(\text{NO}_x)$  emitted by biomass combustion and the  $\delta^{15}\text{N}$  of the burnt vegetation:  $\delta^{15}\text{N}(\text{NO}_x) = 0.98 \times \delta^{15}\text{N}_{\text{biomass}} + 1.7$ . Regarding the  $\delta^{15}\text{N}_{\text{biomass}}$  value, we decided to

take the average value given by Martinelli et al. (1999),  $(-2.8 \pm 2.0)$  ‰ which represents an average over a large number of  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}(\text{NO}_x)$  and  $\delta^{15}\text{N}_{\text{biomass}}$ , and combined their work with that of Fibiger and Hastings (2016) to obtain a new linear relationship, namely:  $\delta^{15}\text{N}(\text{NO}_x) = (0.42 \pm 0.17) \times \delta^{15}\text{N}_{\text{biomass}} + 1.3$ . Therefore, in order to account for more recent studies, we propose to use this relationship to derive a new mean value of biomass combustion  $\delta^{15}\text{N}(\text{NO}_x)$ , which is now at  $(0.1 \pm 1.3)$  ‰, which is anyway very close to our initial value. More details are given in the revised manuscript as (lines 689-693):

“ $\delta^{15}\text{N}$  of  $\text{NO}_x$  released during biomass combustion is primarily driven by the  $\delta^{15}\text{N}$  of the biomass burnt (Fibiger and Hastings, 2016). We estimate an average  $\delta^{15}\text{N}$  of biomass combustion  $\text{NO}_x$  at  $(-0.1 \pm 1.3)$  ‰, using the empirical relationship of Chai et al. (2019) (which was derived from combustions of several North American wood species) and an average  $\delta^{15}\text{N}$  of biomass at  $(-2.8 \pm 2.0)$  ‰ 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  $\text{N}_2\text{O}_5$  pathway and using the expression of the EIE fractionation factor between  $\text{N}_2\text{O}_5$  and  $\text{NO}_2$  given by Walters and Michalski (2015) (Appendix D) constrained with the mean nighttime temperature at our site, the isotopic composition of  $\text{NO}_3^-$  is expected be enriched in  $^{15}\text{N}$  by about 29 ‰ compared to  $\text{NO}_2$ . This estimated  $^{15}\text{N}$  enrichment is about three times higher than the observed  $\Delta^{15}(\text{NO}_3^- - \text{NO}_2)$  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

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