

Zheng et al., showed that volatile organic compounds play a critical role in the nitrate production on a plateau city, as inferred from the oxygen isotope anomaly of nitrate ($\Delta^{17}\text{O}-\text{NO}_3^-$). The $\Delta^{17}\text{O}-\text{NO}_3^-$ hold a wealth information about the atmospheric oxidation environment, which can be used to complement the model work as an observational constraint for NO_x chemistry. I believe this study is of significant importance to the community as there are very sparse measurements of oxygen isotope anomaly of nitrate in high-elevation plateau environments. While I agree with most of the interpretation, some of the results, i.e., the day-night difference in $\Delta^{17}\text{O}-\text{NO}_3^-$ require further deliberation. In addition, considerable improvements could be made in the presentation of the results, refining the methodology, the layout of the figures, as well as enhancing the overall clarity of the writing. Overall, the manuscript should be subjected to major revisions listed below.

Response: We would like to express our deepest gratitude for the constructive comments, which have significantly improved the quality of our work. Below, we provide detailed, point-by-point responses to all the reviewers' comments. All the changes have been included in the newest manuscript (Reviewers' and Editorial Office's comments are in italics; our responses are in regular font).

Specific comments:

1: The author highlights that $\text{VOCs}+\text{NO}_3$ is of particular important for nitrate formation in Lhasa in spring based on the $\Delta^{17}\text{O}$ measurements and a simple mass-balance model calculation (i.e., Bayesian). The author did a lot of statistical analysis based on the Bayesian model outputs. It is well known that the Bayesian models of this nature was mathematically underdetermined and there was no unique solution with only one constraint but for three solutions (see Phillips et al., 2014), therefore model results will be associated with significant uncertainty. The comparison, statistical analysis and any conclusions draw from these results should be approached with great caution. For example, the contribution of $\text{OH}+\text{NO}_2$ likely

fluctuates around 50% throughout the year.

Response: Thanks for your valuable suggestion. We fully acknowledge that Bayesian isotope mixing model (SIAR) used in our study is mathematically underdetermined when constrained by a single tracer ($\Delta^{17}\text{O}-\text{NO}_3^-$) and three potential pathways, as discussed in Phillips et al. (2014). As a result, the output carries inherent uncertainty, and the exact source apportionment solutions are not unique.

To assess the robustness of our findings, we conducted a sensitivity analysis by varying two key parameters: (1) α , the fraction of NO_2 oxidized by O_3 , and (2) $\Delta^{17}\text{O}$ of terminal O atoms in O_3 ($\Delta^{17}\text{O}-\text{O}_3^*$). As shown in Table S1, both parameters influence the partitioning results. When $\Delta^{17}\text{O}-\text{O}_3^*$ was fixed at 39‰, increasing α from 0.7 to 0.9 led to a substantial increase in the contribution of the $\text{NO}_2 + \text{OH}$ pathway (from 25% to 46%), while the $\text{NO}_3 + \text{VOC}$ pathway decreased (from 46% to 25%). In contrast, the $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ contribution remained nearly constant at 28-29%, indicating its relative insensitivity to α .

Similarly, when α was set between 0.8-0.9, increasing $\Delta^{17}\text{O}-\text{O}_3^*$ from 37‰ to 39‰ resulted in a rise in the $\text{NO}_2 + \text{OH}$ contribution (from 37% to 46%) and a decline in $\text{NO}_3 + \text{VOC}$ (from 35% to 26%), while the $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ pathway again remained stable. These results suggest that although the $\text{NO}_2 + \text{OH}$ and $\text{NO}_3 + \text{VOC}$ pathways are sensitive to assumptions about α and $\Delta^{17}\text{O}-\text{O}_3^*$, the $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ pathway is relatively robust across the tested range.

Given that Lhasa is characterized by relatively high VOC concentrations and that $\Delta^{17}\text{O}-\text{O}_3^*$ is typically close to 39‰, we believe that our parameter assumptions are reasonable.

To address your concern, we have carefully revised the main text to avoid overstatements and now use more cautious language when discussing model-derived pathway contributions. **(Line 333-348)**

Line 333-348: To evaluate the impact of key parameters on the estimated contributions of different NO_3^- formation pathways, we conducted a sensitivity analysis by assumed the α values and $\Delta^{17}\text{O}$ value of the terminal oxygen atoms of O_3 ($\Delta^{17}\text{O}-\text{O}_3^*$). As listed in Table S3, the assumption of α and $\Delta^{17}\text{O}-\text{O}_3^*$ have an impact on the NO_3^- formation

mechanisms. When $\Delta^{17}\text{O}-\text{O}_3^*$ was fixed at 39‰, increasing α from 0.7 to 0.9 led to a notable increase in the relative contribution of the $\text{NO}_2 + \text{OH}$ pathway from 25% to 46%, while that of the $\text{NO}_3 + \text{VOC}$ pathway decreased from 46% to 25%. The $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ pathway remained nearly constant, with contributions ranging between 28% and 29%, indicating that this pathway is relatively insensitive to changes in α values. Similarly, when α was varied within a reasonable range (0.68-0.93), increasing the $\Delta^{17}\text{O}-\text{O}_3^*$ value from 37‰ to 39‰ led to an increase in the $\text{NO}_2 + \text{OH}$ contribution from 37% to 46%, and a corresponding decrease in the $\text{NO}_3 + \text{VOC}$ contribution from 35% to 26%. Again, the $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ contribution remained stable at $\sim 28\%$. These results suggest that the estimated contributions of $\text{NO}_2 + \text{OH}$ and $\text{NO}_3 + \text{VOC}$ pathways are sensitive to assumptions about α and $\Delta^{17}\text{O}-\text{O}_3^*$, whereas the contribution of the $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ pathway is relatively robust under the tested conditions. Because Lhasa is characterized by relatively high VOC concentrations and $\Delta^{17}\text{O}-\text{O}_3^*$ is generally close to 39‰ in the troposphere, we consider our parameter assumptions reasonable for further estimating NO_3^- formation pathways for each sample.

Table S3 The average contribution of three oxidation pathways to NO_3^- formation for the different the α values and $\Delta^{17}\text{O}-\text{O}_3^*$ values

parameters	relative contribution of different oxidation pathways (%)		
	NO_2+OH	NO_3+VOC	$\text{N}_2\text{O}_5+\text{H}_2\text{O}$
<u>$\Delta^{17}\text{O}-\text{O}_3^*=39\text{‰}$</u>			
$\alpha=0.7$	25	47	28
$\alpha=0.8$	41	29	30
$\alpha=0.9$	46	26	28
<u>$\alpha=0.68-0.93$</u>			
$\Delta^{17}\text{O}-\text{O}_3^*=37\text{‰}$	37	35	28
$\Delta^{17}\text{O}-\text{O}_3^*=38\text{‰}$	42	30	28
$\Delta^{17}\text{O}-\text{O}_3^*=39\text{‰}$	46	26	28

2: Regarding the source of VOCs, the authors suggest that high ambient VOCs in spring may originate from South Asia via long-range transport. There are growing evidence that long-range transport of atmospheric pollutants from South Asia regulating the aerosol loadings in south of Tibetan Plateau in spring. Does nitrate aerosol in Lhasa also be impacted by the long-range transport, especially in spring? It is likely that the author assumed that long-range transported VOCs involve in the local nitrate production in Lhasa through $\text{NO}_3 + \text{VOC}$ pathways. This should be explicitly addressed in the main text.

Response: Thanks for your insightful comment. As suggested, we have revised the main text to explicitly clarify the potential influence of long-range transported VOC on NO_3^- formation in Lhasa, particularly during spring. We highlight that air masses originating from South Asia (e.g., Afghanistan, Pakistan, northern India, Nepal) during spring are likely to carry biomass burning-related VOC, which could enhance local NO_3^- formation via the $\text{NO}_3 + \text{VOC}$ pathway. We have also noted that elevated ambient VOC levels in urban areas on the Qinghai-Tibet Plateau, comparable to those in the North China Plain, may be further amplified by this long-range transport. Furthermore, we acknowledged the potential co-transport of nitrogenous species (e.g., NO , NO_2) associated with biomass burning that could also contribute to NO_3^- formation. **(Line 410-440)**

Line 410-440: A significant increase in the $f_{\text{NO}_3 + \text{VOC}}$ values was observed in spring ($p < 0.05$). First, O_3 and NO_2 are precursors of NO_3 . In this work, the highest concentrations of O_3 were found in spring ($114.9 \pm 18.1 \mu\text{g}/\text{m}^3$), likely leading to elevated NO_3 concentrations. Additionally, the low temperature and reduced OH radical concentrations in spring facilitate the reaction of NO_2 and O_3 to synthesize NO_3 . This might be an appropriate reason for the $f_{\text{NO}_3 + \text{VOC}}$ values in spring. High-altitude locations such as Nepal (5079 m a.s.l.) and Qomolangma Station (4300 m a.s.l.) have experienced stratospheric ozone intrusions, especially in spring and winter, as reported in previous studies (Zhang et al., 2025; Cristofanelli et al., 2010; Morin et al., 2007; Zhang et al., 2022; Lin et al., 2016; Yin et al., 2017; Wang et al., 2020b). Notably, such intrusions in spring may elevate tropospheric O_3 levels in Lhasa, resulting in a mixture

of tropospheric and stratospheric O_3 that enhances NO_3^- production. Second, previous study has indicated that the Afghanistan-Pakistan-Tajikistan region, the Indo-Gangetic Plain, and Meghalaya-Myanmar region could transport industrial VOC to various zones in Tibet from west to east. Additionally, agricultural areas in northern India could contribute biomass burning-related VOC to the middle-northern and eastern regions of Tibet (Li et al., 2017). During our sampling campaign, South and Southeast Asia air clusters were notably prevalent in the springtime, coinciding with intensive fire spots observed in Afghanistan, Pakistan, India, Nepal, and Bhutan (Figure S3/S4). These observations, combined with the prevailing South and Southeast Asia air mass trajectories in spring, strongly suggest that long-range transported VOC from South Asia were delivered to Lhasa and likely participated in local NO_3^- production via $NO_3 + VOC$ pathway. Moreover, recent studies have shown that ambient VOC concentrations in the urban areas on the Qinghai-Tibet Plateau were comparable to those in the North China Plain (Tang et al., 2022). The input of VOC through long-range transport might further elevate VOC concentrations, thereby promoting NO_3^- formation via $NO_3 + VOC$ pathway and contributing to the enhanced f_{NO_3+VOC} values observed in spring. While VOC appears to play a dominant role in the process, it should be noted that other nitrogen species (e.g., NO, NO_2) associated with biomass burning emissions may also be transported over long distances and influence NO_3^- formation in Lhasa. These co-transported nitrogen compounds, although not directly quantified in this study, could further contribute to NO_3^- production in spring. Taken together, these findings provide strong evidence that long-range transport of biomass burning emissions, particularly from South Asia, can substantially influence springtime NO_3^- formation in Lhasa.

3: (1) The methodology for the determination of specific pathway contribution to nitrate based on $\Delta^{17}O$ should be clearly presented in the Method section. One of the most important of part is the A value (i.e, the relative importance of O_3 versus RO_2 in NO_2 formation), when using $\Delta^{17}O$ to distinguish nitrate formation pathways. First, I noticed that the author derived the RO_2 concentrations based on a empirical

relationship about O₃ mixing ratio. This relationship between RO₂ and O₃ indeed has been widely used in relevant study as concurrent RO₂ measurement is unavailable. This method is feasible at present. However, the relationship between RO₂ and O₃ the author used in this study is referred to Kanaya et al., 2007, which was conducted in urban site in central Tokyo. I believe that the atmospheric condition in Lhasa is completely different from that in Tokyo, i.e., the dominant RO₂ source. RO₂ production is majorly determined by solar radiations, which is also different between the two sites, as noticed in the Introduction. I recommend the calculation of RO₂ concentrations using MCM model and recent field observations of VOCs at Lhasa (see Chunxiang Ye et al., 2023).

Response: Thanks for your valuable suggestion. We sincerely thank the reviewer for pointing out the importance of accurately estimating RO₂ concentrations in the calculation of the α value, which is indeed a critical parameter for $\Delta^{17}\text{O}$ -based pathway apportionment. As noted, we adopted an empirical relationship between RO₂ and O₃ based on Kanaya et al. (2007), due to the absence of direct RO₂ observations and the lack of local model constraints. We fully acknowledge that this parameterization, developed for urban Tokyo, may not fully reflect the atmospheric conditions in high-altitude Lhasa, particularly given differences in radiation intensity and VOC composition.

Unfortunately, due to the lack of comprehensive VOC datasets and the necessary input parameters, we were unable to conduct a robust MCM (Master Chemical Mechanism) simulation for RO₂ in this study. We agree that such modelling, particularly with reference to recent VOC measurements in Lhasa, would significantly improve the accuracy of pathway estimation. We will prioritize this in our future work as more data becomes available.

(2) Second, the author also suggests that nighttime RO₂ may play a role in the NO_x oxidations. Similarly, the derivation of nighttime RO₂ is valid only when O₃ oxidation VOC dominates the RO₂ production (Kanaya et al., 2007). Nighttime RO₂ production mechanisms in Lhasa maybe unknown, however, in other urban cities such as

Beijing in China, NO_3 radical + VOC is the dominant channel for nighttime RO_2 production. In this case, nighttime RO_2 will be roughly correlated with the NO_3 radical production rate, $k_{\text{O}_3+\text{NO}_2}[\text{O}_3]/[\text{NO}_2]$. Although, given the high nighttime O_3 concentration in Lhasa, it maybe reasonable to assume O_3 dominant nighttime NO oxidation. To improve the robustness of the pathway differentiation, I recommend that this part could be done according to the approach of Alexander et al., 2020, and compare the field $\Delta^{17}\text{O}-\text{NO}_3^-$ measurements with the model results in Alexander et al., 2020.

Response: Thanks for your insightful comment. Following your suggestion, we have further elaborated on the potential role of nighttime RO_2 in NO_3^- formation in Lhasa and its possible link to $\text{NO}_3 + \text{VOC}$ pathway. Although the exact mechanism of nighttime RO_2 production in Lhasa remains uncertain, previous studies have identified $\text{NO}_3 + \text{VOC}$ reactions as the dominant source of RO_2 during nighttime. This process forms alkyl and multifunctional nitrates (RONO_2), which can undergo hydrolysis to yield HNO_3 , contributing to NO_3^- production. We also acknowledge the importance of O_3 and NO_2 in controlling the nighttime NO_3 radical production rate. Given that nighttime O_3 concentrations in Lhasa are relatively high, it is plausible that NO_3 radical levels are also elevated, enhancing $\text{NO}_3 + \text{VOC}$ pathway. We have added it to the revised manuscript. **(Line 351-388)**

Line 351-388: On average, the relative contributions of $\text{NO}_2 + \text{OH}$ ($f_{\text{NO}_2+\text{OH}}$), $\text{NO}_3 + \text{VOC}$ ($f_{\text{NO}_3+\text{VOC}}$) and $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ ($f_{\text{N}_2\text{O}_5+\text{H}_2\text{O}}$) to NO_3^- formation in Lhasa during the sampling campaign were $46 \pm 26\%$, $26 \pm 19\%$ and $28 \pm 11\%$, respectively. To better understand the characteristics of NO_3^- formation mechanism in Lhasa, we performed a detailed comparison around the China for the relative contributions of key oxidation pathways using the $\Delta^{17}\text{O}$ methodology (Figure 4). Overall, similar to most Chinese cities, NO_3^- formation in Lhasa was predominantly driven by the $\text{NO}_2 + \text{OH}$ pathway, exhibiting distinct seasonal and regional variations. In particular, the average $f_{\text{NO}_3+\text{VOC}}$ values were generally several times higher in spring in Lhasa than in other urban cities. Compared to rural/remote areas, the average $f_{\text{NO}_3+\text{VOC}}$ values showed higher fractions in Lhasa, revealing the influence of anthropogenic emission, i.e., vehicle exhaust and

heating, on NO_3^- formation. In Lhasa, the Capital of Tibet, field measurements among different years showed a substantial increase in VOC concentrations in urban areas of the Tibet Plateau, comparable to those in North China (Tang et al., 2022), revealing the importance of the active $\text{NO}_3 + \text{VOC}$ pathway for NO_3^- pollution formation in Lhasa. In fact, recent studies have recognized $\text{NO}_3 + \text{VOC}$ as a major formation mechanism for NO_3^- production. For instance, Fan et al. (2021) found that $f_{\text{NO}_3+\text{VOC}}$ in Beijing increased from 17% in summer to 32% in winter based on $\Delta^{17}\text{O}-\text{NO}_3^-$ measurements. . He et al. (2018) estimated the relative contributions of $\text{NO}_3 + \text{VOC}$ and $\text{N}_2\text{O}_5 + \text{Cl}^-$ to NO_3^- formation and found that $\text{NO}_3 + \text{VOC}$ and $\text{N}_2\text{O}_5 + \text{Cl}^-$ were in the range of 16-56%, underscoring the significant roles of these pathways during haze events in Beijing. Similarly, Feng et al. (2023) also reported that the $f_{\text{NO}_3+\text{VOC}}$ values were up to 49.6% in winter in northern China. In Guangzhou,, Wang et al. (2023) noted that the average $f_{\text{NO}_3+\text{VOC}}$ value was at the 488m (25%) higher than that at the ground (12%). Furthermore, Li et al. (2022) reported that $f_{\text{NO}_3+\text{VOC}}$ increased from 5% in urban to 13.5% in rural regions in Northeast China. Although the specific nighttime RO_2 production mechanism in Lhasa remains unclear, studies in other cities have demonstrated that NO_3+VOC pathway was the dominant channel for nighttime RO_2 (Fisher et al., 2016), which in turn leads to the formation of alkyl and multifunctional nitrates (RONO_2) and eventually NO_3^- . In such cases, the RO_2 concentration is expected to be correlated with NO_3 radical production, which depends on the reaction rate of O_3 and NO_2 (Brown and Stutz, 2012). Given the relatively high nighttime O_3 concentrations in Lhasa, it is plausible that O_3 -driven nighttime NO_3 chemistry plays an important role, thereby enhancing NO_3+VOC derived from RO_2 production and NO_3^- formation. Global modelling studies also support the significant of this pathway. For instance, Alexander et al. (2020) reported that the $\text{NO}_3 + \text{VOC}$ pathway via the RONO_2 mechanism accounted for 3% of global NO_3^- formation on average. The relatively high $f_{\text{NO}_3+\text{VOC}}$ values observed in Lhasa are broadly consistent with these findings, especially under conditions of high VOC concentrations and strong nighttime oxidant levels.

4: I DONOT agree with the interpretation of the observed day-night differences in $\Delta^{17}\text{O}-\text{NO}_3^-$ during winter and summer (Lines: 307-333). Remember that daytime NO_3 and N_2O_5 chemistry should be negligible in nitrate chemistry, and no supporting evidence for this claim could be found in reference in Brown et al., 2011. Note high NO_3 production rate not means high mixing ratio of NO_3 , NO_3 and N_2O_5 will be rapidly decomposed under sunlight. Although there are increasing studies showing the potential impact of daytime NO_3 radical chemistry, the importance of daytime $\text{NO}_3/\text{N}_2\text{O}_5$ chemistry should be investigated with concurrent field observations or model experiments. The atmospheric residence time of nitrate should be considered for the comparison of day-night difference in $\Delta^{17}\text{O}-\text{NO}_3^-$, see Vicars et al., 2013.

Response: Thanks for your valuable suggestion. Specifically, we acknowledge that under typical atmospheric conditions, NO_3 and N_2O_5 are rapidly photolyzed during the day, with reported NO_3 lifetimes of less than 10 seconds in sunlight, making their daytime accumulation negligible. However, we also note that several recent studies suggest that daytime NO_3 production rates can be non-negligible, especially in winter. To address the reviewer's concern, we have clarified the distinction between production rate and ambient concentration, and we now explicitly acknowledge the uncertainty in the role of daytime $\text{NO}_3/\text{N}_2\text{O}_5$ chemistry. Additionally, we now consider the atmospheric residence time of nitrate, as recommended (Vicars et al., 2013), which may lead to integrated contributions from both daytime and nighttime chemistry in each sample. **(Line 450-484)**

Line 450-484: Interestingly, distinct diurnal patterns of NO_3^- oxidation pathways were observed during the sampling campaign (Figure 5). In summer, $\text{NO}_2 + \text{OH}$ pathway showed a significantly higher contribution during the daytime (55.1%) compared to nighttime (44.9%), which is attributed to increased OH radical synthesis during longer days and higher temperatures in Lhasa (Rohrer and Berresheim, 2006). A previous study indicated that lower NO_2 and higher O_3 concentrations enhance the relative contribution of OH pathway to NO_3^- formation (Wang et al., 2019). Additionally, the concentration of ALWC (the detailed information is given in Text S3) was higher at night than during the day in summer, favoring NO_3^- formation through nocturnal

formation. In winter, $f_{\text{NO}_2+\text{OH}}$, $f_{\text{NO}_3+\text{VOC}}$ and $f_{\text{N}_2\text{O}_5+\text{H}_2\text{O}}$ were similar during both day and night. Typically, photolytic destruction and chemical reactions with NO are rapid sinks during the daytime, with lifetimes generally less than 5 seconds and resulting in extremely low concentrations. Similarly, the atmospheric lifetime of N_2O_5 under sunlight is also very short (Wang et al., 2018). Thus, daytime NO_3 and N_2O_5 chemistry is often considered negligible. However, a recent study revealed that a non-negligible amount of NO_3 radicals can persist during the daytime in cold months, owing to the limited solar radiation (Hellén et al., 2018). Wang et al. (2020a) found that the daytime production rate of NO_3 can be substantial due to elevated concentrations of O_3 and NO_2 , suggesting that the mixing ratios of NO_3 and N_2O_5 during the day may not be negligible. Furthermore, in winter, lower temperatures and elevated NO_2 concentrations facilitate a quasi-steady-state equilibrium between NO_3 and N_2O_5 , slowing the overall reactivity of the NO_3^- precursors (Brown et al., 2003). This equilibrium condition minimizes diurnal fluctuations in precursor concentrations, resulting in relatively stable nocturnal and daytime NO_3^- formation pathways, including $\text{NO}_3 + \text{VOC}$ and $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$. Nevertheless, we acknowledge that the exact role of daytime $\text{NO}_3/\text{N}_2\text{O}_5$ chemistry remains uncertain in Lhasa and should be further assessed using concurrent field observations or chemical transport models. Moreover, when interpreting the diurnal differences in $\Delta^{17}\text{O}-\text{NO}_3^-$ values, the atmospheric lifetime of NO_3^- must be considered. Given the atmospheric lifetime of NO_3^- is generally more than 12 hours, each sample might reflect both daytime and nighttime NO_3^- production impacting on $\Delta^{17}\text{O}-\text{NO}_3^-$ values (Park et al., 2004; Vicars et al., 2013).

General comment

1: The description of nitrate formation pathways (Text S1) and the associated $\Delta^{17}\text{O}$ signatures should be presented in the main text.

Response: Thanks for your suggestion. We have added it to the main text in the revised manuscript (2.4).

2: Line 62-63 Numerous field experiments have demonstrated that the N_2O_5 uptake probability on aerosol varied significantly, depending on the aerosol composition, meteorological parameters.

Response: Thanks for your valuable suggestion. We have clarified this point in the revised manuscript by specifying that one of the major sources of uncertainty in modelling NO_3^- formation via the $N_2O_5 + H_2O$ pathway is the wide variability in the N_2O_5 uptake probability (γ), which has been shown in numerous field experiments to depend strongly on aerosol composition and meteorological conditions such as temperature and relative humidity. **(Line 72-75)**

Line 72-75: However, there is considerable uncertainty in modelling the contribution of individual oxidation pathways to NO_3^- formation, particularly for the $N_2O_5 + H_2O$ pathway, due to the wide variability of key parameters such as the N_2O_5 uptake coefficient, which has been shown to vary significantly with aerosol composition, relative humidity, and temperature.

3: Line 237: I think the highlight of the text is the comparison of nitrate chemistry in high-elevation city with that in plain region. More discussion is needed to explore the mechanisms regulating the nitrate oxidation pathways, rather than a simple comparison of relative importance.

Response: Thanks for your suggestion. Specifically, we have expanded the discussion to include potential mechanisms that may regulate the observed differences in oxidation pathways, with a particular focus on the $NO_3 + VOC$ pathway. In this context, we discuss the role of elevated nighttime O_3 concentrations in Lhasa. Since this issue overlaps with the reviewer's Specific Comment 3 regarding the role of nighttime RO_2 and the importance of linking NO_3 radical production to ambient oxidant levels, we addressed both concerns together in the revised discussion to provide a more robust and coherent mechanistic interpretation.

4: Line 345-347 Recent field radical measurements in urban sites in China found that OH and HO2 radical during haze period is comparable to clean days, see Slater

et al., 2020, Lu et al., 2019.

Response: Thanks for your suggestion. We sincerely apologize for not citing the most up-to-date literature in our original manuscript. Initially, we referred to earlier studies, which may have led to an outdated understanding of radical behavior under polluted conditions. In response to the reviewer's helpful comment, we have carefully reviewed recent findings and incorporated updated references (Slater et al., 2020; Yang et al., 2021), which indicate that OH and HO₂ radical levels during haze periods can be comparable to those on clean days in urban China. We have revised the manuscript.

(Line 502-511)

Line 502-511: As shown in Figure S8, NO₃ + VOC pathway emerged as the major contributor to NO₃⁻ formation during periods of high NO₃⁻ spikes. To elucidate the NO₃⁻ formation pathways under different NO₃⁻ concentrations, NO₃⁻ samples were categorized into different concentration ranges (Figure 6). We found the $f_{\text{NO}_3+\text{VOC}}$ values increased and $f_{\text{NO}_2+\text{OH}}$ values decreased with the NO₃⁻ concentrations. Although recent field radical measurements in urban sites in China found that OH and HO₂ radical during haze period is comparable to clean days (Slater et al., 2020; Yang et al., 2021), our results suggested that NO₃+VOC pathway still played an important role in NO₃⁻ production under high-NO₃⁻ concentration in Lhasa, possibly due to enhanced VOC emission.

5: Line 373 *The implication sounds impotent. It is well known that aerosol liquid water content (ALWC) and Ox (oxidation capacity) regulate nitrate concentrations—ALWC impacts gas-to-particle partitioning, while Ox affects oxidation efficiency. The authors should focus on the specific or unique environmental conditions in the Tibetan Plateau that could be reflected by the measurements of $\Delta^{17}\text{O}-\text{NO}_3^-$.*

Response: Thanks for your suggestion. We have strengthened the Implications section to better highlight the unique environmental conditions of the Tibetan Plateau, particularly those that influence nitrate oxidation as captured by $\Delta^{17}\text{O}-\text{NO}_3^-$. Specifically, we now emphasize the role of high solar radiation, persistently elevated O₃ levels, and seasonally enhanced VOC concentrations in Lhasa, which together

promote active $\text{NO}_3 + \text{VOC}$ chemistry — especially in spring. These features are characteristic of high-altitude urban environments and contribute to the distinct oxidation pathways observed in this region.

At the same time, we acknowledge the limitations of our study. Due to the lack of direct observations of RO_2 concentrations in Lhasa, we adopted empirical estimations based on other regions, which introduces uncertainty into the pathway apportionment. Additionally, the absence of measurements related to nighttime NO emissions and NO_2 -NO isotope exchange in the region may affect the accuracy of the diurnal pattern interpretation. We have added these points to the revised Implications section to clarify the scope and robustness of our conclusions. **(Line 540-559)**

Line 540-559: The oxidation pathways of NO_3^- in Lhasa, China, were constrained using a full year of $\Delta^{17}\text{O}-\text{NO}_3^-$ measurements from 2022 to 2023. Based on seasonal data, we observed a significant increase in the relative contribution of the $\text{NO}_3 + \text{VOC}$ to NO_3^- formation during spring. Furthermore, the diurnal distribution of NO_3^- oxidation pathways varied distinctly across seasons. To better understand the factors influencing these pathways, we integrated meteorological conditions, NO_x precursors, and ALWC for a more comprehensive analysis of NO_3^- formation. The results revealed that Ox and ALWC are more reliable indicators of NO_3^- oxidation pathways than meteorological factors. Notably, Lhasa's unique high-altitude environment such as strong solar radiation, persistently high O_3 , and seasonally elevated VOC, promotes active $\text{NO}_3 + \text{VOC}$ chemistry, especially in spring. Atmospheric ALWC is primarily produced by hygroscopic aerosols such as SO_4^{2-} , NH_4^+ , and Cl^- . Therefore, in addition to controlling NO_2 , O_3 , and VOC, reducing these hygroscopic aerosols is crucial for effective $\text{PM}_{2.5}$ pollution control.

Although this study provides valuable insights into NO_3^- formation mechanisms in Lhasa, we must acknowledge the associated uncertainties due to the lack of comprehensive observational constraints in Lhasa. Specifically, the limited understanding of local RO_2 concentrations led us to adopt empirical parameterizations and refer to measurements from other regions, which inevitably introduce uncertainty into the pathway apportionment. In addition, the absence of direct observations of

nighttime NO emissions and the NO₂-NO isotope exchange processes in this region further complicates the interpretation of diurnal variations in NO₃⁻ formation pathways. To improve the robustness of $\Delta^{17}\text{O}$ -based pathway analysis, future studies should consider synchronous measurements of both NO₂ and NO₃⁻ isotopes.

6: Additionally, many sentences throughout the manuscript require careful revision for clarity and grammar (e.g., Lines 31–33)

Response: Thanks for your suggestion. We have carefully reviewed and revised the entire manuscript to improve the clarity, grammar, and overall readability of all sentences, including the example in Lines 31–33.

Reference

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