Response to Reviewer #2's comments

The manuscript by Chai et al. reports on ground-based measurements of isotopic ratios ($^{15}N/^{14}N$) and ($^{18}O/^{16}O$) and concentrations of NO_x and HONO derived from fresh and aged wildfire smoke plumes. Measurements were conducted from several locations in the Western U.S. during the WE-CAN and FIREX-AQ field campaigns using state-of-the art measurement techniques. Furthermore, the data is presented and assessed thoroughly to the full extent that the data allows. This is a significant contribution for the following reasons: It reports for the first time the isotopic ratios of HONO in wildfire plumes and the isotopic evidence is used to evaluate the relative importance of various HONO formation/loss pathways (homo- and heterogeneous) that have until now only been studied in the laboratory or invoked with considerable speculation. Thus, I feel this work contributes significantly because it provides in situ insights into which HONO formation and loss processes are important in wildfire smoke plumes. In addition, the authors present a simple but elegant box model for assessing the importance of these pathways, that can be useful in future studies aimed at studying atmospheric processes involving reactive nitrogen. The paper is not without its weaknesses. Most significantly, many of the parameters needed to model (e.g., the enrichment factors) are not well constrained. However, the authors use well-reasoned assumptions and qualify their estimates by clearly discussing the limitations in the extensive appendices to the manuscript. Overall, I feel this is not a deal-breaker since these are the best estimates that can be made using the available data (none of the enrichment factors have been evaluated in the literature). I feel this manuscript should be published in ACP after the following specific points have been addressed.

We really appreciate the careful read, positive feedback and encouragement from Reviewer 2. Below we respond to the reviewer's specific comments point by point in blue text.

The more significant questions in my reading of the work have to do with how HONO is modeled. If I am not mistaken, the isotopic model uses reactions R1-R4 for daytime chemistry and reactions R5-R7 to represent the nighttime chemistry controlling the HONO isotopic signature. In reality, reactions R5-R7 are also occurring during the daytime and could be important. For example, modeling studies often find that good agreement between model and measured HONO concentrations is only possible when deposition processes are included during the daytime (in addition to photolysis). Particle scavenging in smoke events will be particularly important due to the added surface area provided by particulate matter/smoke particles. For the same reason, non-photochemical sources such as R6 will occur during both the night and daytime. I feel it would be useful for the authors to justify their decision to omit reactions R5-R7 in the modeled daytime results. I also wonder how reliable the models results are with respect to distinguishing between Reactions (R6) and (R7)? That is, it was not clear how the parameterization of these two reactions was different and whether, due to the level of uncertainty associated with the enrichment factors and mechanisms, whether it is even possible to distinguish between them, especially since the relative contribution of R6 may be so low. Modern laboratory experiments (and theory) conducted under atmospherically relevant conditions suggest that reaction R6 is only important at very high (>100 ppbV) NO_2 concentrations when dimerization is favored. Measured NO_2 concentrations in this study were below 20 ppbV, so I would have my doubts that NO_2 levels were high enough to favor any NO_2 hydrolysis. In addition, in section B.1.2., I agree that HONO desorption involving breaking of the complex HONO...$(H_2O)_n$ is likely important for determining KIF. I note that the distinction between the heterogeneous NO_2 reactions (R3, R6, and R7) is the role of water. In R3 & R7, H_2O is the medium, while in R6 H_2O is both reactant and medium, so would one not expect R6 to have a very different enrichment factor compared to R3 and R7?

Thank you for raising these concerns, which are important points to be considered.

First, we agree deposition of HONO could be an important sink during the day. In fact, we have estimated the relative importance of HONO deposition on the ground compared to daytime HONO photolysis. The deposition coefficient (k_d) was calculated following equation $\boldsymbol{k_d = v_{HONO}/H}$, where v_{HONO} is the dry deposition velocity and it is assumed to be 0.008 m s^{-1} (Nie et al., 2015), and H is the daytime boundary layer height with a range of 1000-3000 m (Zhang et al., 2020). Taking an average of HONO photolysis coefficient of 0.001 s^{-1}, HONO lost to deposition is less than 1% that lost to photolysis. Similarly, HONO lost to OH+HONO and particle uptake is at the same magnitude of deposition. As such in the manuscript we state photolysis is the dominant loss pathway for HONO.

Second, for N isotopic fractionation associated with HONO production, R3, R6 and R7 are not distinguishable because the kinetic processes are all expected to be controlled by a desorption step, as discussed in lines 636-639: "Kinetic isotopic fractionation (KIF) associated with photo-enhanced NO_2 conversion is not known. Similar to the nighttime heterogeneous NO_2 conversion, R3 is also expected to occur in the surface aqueous phase and the overall KIF is largely determined by that associated with the desorption of HONO from aqueous to gas phase. Thus, $^{15}\varepsilon_3$ and $^{18}\varepsilon_3$ are the same as that of R6 and R7 (Appendix B.1.2)."

From our model and the parameterization for N isotopes, there is not a satisfying way to distinguish R3 and R7 during the daytime. However, we are currently undertaking a series of laboratory studies that aims to characterize if these two reactions can be distinguished via N isotopic fractionation. Thus, we cannot rule out the importance of R7 during the daytime with the current parametrization. In order to address this concern, we have added the text in lines 373-381: "However, there are two limitations to the modeling results. First, as the $^{15}N/^{14}N$ fractionation associated with R3, R6 and R7 are not distinguishable with our current parameterization (Appendix B.1.2 and B.2.2), we cannot rule out the potential importance of heterogeneous NO_2-to-HONO conversions (R6 and R7) in daytime. Second, it should be noted that the results represent our best estimate of the average relative importance of R2-R4 for HONO production during our HONO sampling periods (2-10 hours) for the aged daytime plume. Due to the long sample integration time, our samples were influenced by both aged smoke and near-background air when the smoke was very diluted. Under the NO_x–limited condition (low NO_x <1 ppbv) in remote background air, nitrate photolysis is expected to be the major secondary HONO source (Ye et al., 2016; Zhou et al., 2011), which cannot be ruled out by our results. Isotopic measurement techniques with higher time resolution will be required to achieve real-time quantification of the HONO budget."

Third, although R6 and R7 cannot be distinguished by N isotopes, the O isotopic signature can be used to distinguish these processes based upon different reaction mechanisms (i.e., oxygen transfer). In lines 326-327, we explained "For $\delta^{18}O$-HONO, we also took into account transferring effect of oxygen from different O-containing reactants that produce HONO (as explained in Appendix B)". In lines 334-336, we explained "in addition to kinetic isotopic fractionation, the transferring of $\delta^{18}O_{i,t}$ (Eq. (3)) in the reactant (OH, NO, NO_2, H_2O, and NO_3^-) to the product HONO, as HONO contains two O atoms that may stem from more than one reactant (Appendix B)". In lines **409-438** ("The $\delta^{18}O$ signature is subsequently passed to HONO when it is produced from NO (R2) and NO_2 (R3) during the day and from NO_2 (R6 and R7) during the night, … and further indicate the important role peroxy radicals play as an oxidant in wildfire smoke impacted environments."), as well as Figure 6, by combining the modeling results and field observations of $\delta^{18}O$-HONO in aged nighttime smoke, we showed R7 plays a more important role in NO_2-to-HONO conversion. Our result is consistent with the Reviewer's comment that NO_2 hydrolysis is less important in the environments where our measurements were conducted.

My last points have to do with readability of the manuscript and figures. The results and discussion refer extensively to reaction equations (R1-R7) and enrichment factors that are only found in boxes within Figure 1. The text chosen for these reactions is a small serif font placed onto a somewhat busy/distracting background; it is very difficult to read and will be even more so in final published form. Because of their importance, I recommend simplifying Figure 1. For example, consider turning it into a (more boring) black-white scheme that omits the graphics and provides all the relevant equations and numbers in an easy-to-read format. I recommend checking references to equations to ensure they are referring to the correct equations. For example, on lines 650-652, there are references to Eqs. (10)-(12); I believe this should be Eqs. (B10)-(B11).

Thank you very much for the suggestions! We added reactions R1-R7 in the text to make the main text more informative and easier for readers to follow. In the text, we also added the references relevant to each of Equations (10)-(12) separately.

References

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Zhang, Y., Sun, K., Gao, Z., Pan, Z., Shook, M. A., and Li, D.: Diurnal Climatology of Planetary Boundary Layer Height Over the Contiguous United States Derived From AMDAR and Reanalysis Data, J. Geophys. Res. Atmospheres, 125, e2020JD032803, https://doi.org/10.1029/2020JD032803, 2020.