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Comment on acp-2021-225

Anonymous Referee #2

Referee comment on "Isotopic evidence for dominant secondary production of HONO in near-ground wildfire plumes" by Jiajue Chai et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-225-RC2, 2021

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.

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?

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 593-594, there are references to Eqs. (10)-(12); I believe this should be Eqs. (B10)-(B11).