We thank Dr. Jim Roberts (reviewer #1) for his time in reading and reviewing our manuscript, and providing references to review. Below are the point-to-point response to the reviewer #1's comments.

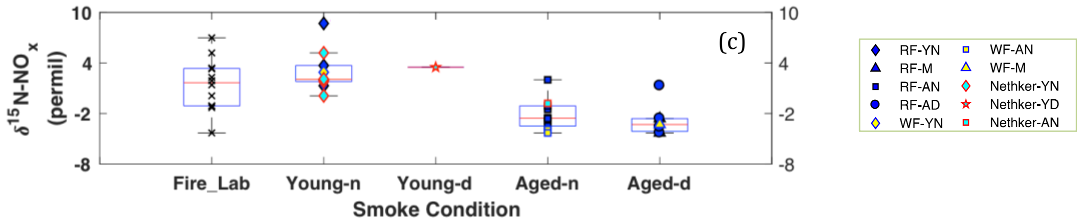
1. Discussion on the interference of PAN with NOx collection system

Thanks for raising these concerns. We acknowledge the strong alkaline solution may trap PAN that would be oxidized by in the permanganate solution to nitrate ion. Agreed that at significant concentrations of PAN, i.e., comparable to that of NOx in the atmosphere, and PAN is collected in the permanganate impinger solution it would interfere with the NOx, also collected as nitrate, for isotopic analysis. However, we do not find significant evidence that this is the case in our study conditions.

There is minimum PAN formed in fresh biomass burning (BB) emissions and young smoke of less than half an hour, based upon previous lab and field measurements, as well as modeling studies (Stockwell et al., 2014; Yokelson et al., 2009; Alvarado et al., 2010, 2015). In aged BB plumes in the upper troposphere, PAN can form rapidly at low temperatures and act as a temporary NOx reservoir, reaching a maximum PAN/NOy ratio of 0.3 (comparable to NOx/NOy) within ~2 to 4 hours of aging after emission (Yokelson et al., 2009; Liu et al., 2016; Akagi et al., 2012). For example, Yokelson et al. (2009) measured smoke from Yucatan fires with PAN/NOy varying from 0.11 to 0.3 (average of 0.18) within 2 hours of aging, and similar results were measured by Liu et al. (2016) for agricultural fires in the southeastern U.S. during SEAC4RS, as well as by Akagi et al. (2012). Note these results are all from airborne measurements.

There are no ground-level measurements for PAN in BB plumes during WE-CAN and FIREX-AQ, nor from other field studies, to best of our knowledge. PAN is thermally unstable in the boundary layer during summertime, and its main loss process in the atmosphere is thermal decomposition to release NO_2. The lifetime of PAN is on the order of 1 hour or less at 20 °C and above (Talukdar et al., 1995; Fischer et al., 2010). We therefore expected PAN in near-ground air to maintain low levels or less due to photochemistry and thermal decomposition. In addition, our samples integrated over 40 min to 2 hours' time scales, and PAN was less likely to interfere with our NOx results.

Furthermore, although no near-ground PAN measurements in BB plumes are available, the isotopic results can also shed some light on whether PAN interference is important in our case. For aged smoke, we would expect δ^{15}N-NOx to decrease from that in fresh emissions due to partial transformation of NOx to additional oxidized N products (e.g. PAN), as well as isotopic exchange between NOx and these oxidized species; both processes will leave ^{15}N depletion in NOx and ^{15}N enrichment in PAN (Walters and Michalski, 2015). If PAN existed at significant concentrations that were 1) comparable with NOx in the atmosphere, and 2) completely collected in the permanganate solution, then the $\delta^{15}N\text{-}NO_3^-$ would reflect the overall δ^{15}N of NOx + PAN in the final reduced permanganate solution. In this case, we would expect that aged smoke would not shift from the δ^{15}N-NOx range of young smoke, because δ^{15}N shifts in both PAN and NOx could offset each other. However, our observed δ^{15}N-NOx mean values for both aged daytime and nighttime smoke are significantly ($p<0.05$) lower than that of the young smoke (shown in the figure below). This ^{15}N depletion in NOx indicates the NOx of aged smoke was the predominant N species collected in the permanganate impinger during our field campaign. Similar analysis was also discussed by Miller et al. (2017).



2. “One of the biggest issues with the analysis is that the airmass classifications (e.g. YN, YD, AN, AD, and MD) are presented here on the basis of the isotope analysis alone. This imparts a bit of a circular logic to the assignment of these classes. A more complete basis for these classifications apparently was presented in the Kaspari et al 2021 reference, so this should be summarized here for support. Also, if they were initially made using the isotopic analysis, then say so and then support those assertions with other data.”

It is an important challenge in our community as to how to define the age of smoke plumes. We had the unique opportunity there to use the oxygen isotopic composition of HONO (δ^{18}O-HONO) to discriminate young versus old smoke because of the isotopic implications of different oxidants/chemistry. In Lines 92-93, we wrote “In this work, we determined the smoke conditions (young vs aged) primarily by comparing the field δ^{18}O-HONO results with that obtained in our previous lab study that represents fresh emissions,…”. In lines 230-243, we presented the approach of using δ^{18}O-HONO to determine young versus aged smoke. For a revised version, we would clarify this approach and include a summary of the analysis in Kaspari et al, 2021, which independently (but still anecdotally) supports our classification based on measurements of other compounds.

3. “The authors use the notation $f^{NO}_{O_3/(O3+RO2)}$, in Equations 4 and 5, but then use $f^{NO}_{O_3/RO_2}$ in the text – are these meant to be the same thing? If so, this is really confusing. It didn’t seem like $f^{NO}_{O_3/RO_2}$ was defined anywhere else, so I had to assume it was the same as the factor define in Equation 5.”

Sorry about the confusion. These are typos and we will correct all of them to be $f^{NO}_{O_3/(O3+RO2)}$

4. “In Figure 1 and associated analysis and discussion around Reactions 6 and 7, the isotope fractionations are the same for both ^{15}N and ^{18}O. How then can this support the statements on Lines 361-362 that R6 and R7 lead to very different d^{18}O values? – this doesn’t make sense on the face of it, and is not at all adequately explained by the material in Appendix B. Is this because of the large difference in d^{18}O for O_3 relative to H_2O? but both reactions 6 and 7 involve NO_2 and (which gets an ^{18}O effect from O_3). This whole phenomenon is just not well explained at all in Appendix B.”

Thank you for the question. δ^{15}N of HONO as a product is predominantly determined by the isotopic fractionation shown in Fig. 1. However, for δ^{18}O, we must consider the transfer of isotopic signals upon reaction as well as potential for fractionation of the isotopes. In appendix B.3, lines 590-601 we discuss how to consider both processes and how we determine the transferring isotope effect(s). This will be further clarified in a revised version.

For your specific question on why “R6 and R7 lead to very different d^{18}O values”, please see lines 593-597, “In R2, OH and NO equally contribute their O-atom to HONO expressed with Eq. (10); In R3 and R7, NO_2 is the exclusive O source of HONO while H_3O^+ only contribute a H^+ to HONO (Ammann et al., 1998; George et al., 2005; Stemmler et al., 2006; Scharko et al., 2017; Kebede et al., 2016); In R6, the hydrolysis mechanism discussed in Appendix B suggests the H_2O-derived OH^- and NO_2-derived $NO^+NO_3^-$ equally contribute their O-atom to HONO (Finlayson-Pitts et al., 2003).”

“Also, the nomenclature in Appendix be is faulty, the reactions B10-12, apparently have mixed subscripts that sometimes denote a chemical (e.g. O_3 =ozone I assume) and sometimes a reaction (e.g. $O_{6,t}$) and what is ‘t’ in these subscripts?”

Thank you for noting this. In Lines 590-591, we wrote “For ^{18}O, in addition to KIF (enrichment factor, ε_O^i *in ‰*), $\delta^{18}O$ transferring from different reactants greatly influence $\delta^{18}O$-HONO ($\delta^{18}O_{i,t}$), especially when the two O atoms of HONO are derived from different reactants.” ‘i’ is reaction number, ‘t’ indicates transfer effect of $\delta^{18}O$. We will add clarification in the text to make this more clear. That said, $\delta^{18}O_{3,t}$ is $\delta^{18}O$ transferring coefficient of R3, where both oxygens in HONO come from NO_2.

5. Nighttime processing of NOx through NO_3 and N_2O_5 can be quite important chemical pathways to HNO_3. Wouldn’t these impart an even large $d^{18}O$ to the NO_3^- and therefore any HONO derived form that nitrate, since those reactions involve 2 molecules of O_3? How would that impact the analysis.

Thank you for raising this question! Indeed, nighttime processing of NOx to HNO_3 is very different from daytime, and this leads to different $\delta^{18}O$ values arising from different isotope transfer effects. When HONO is solely produced from nitrate photolysis, $\delta^{18}O$-HONO would reflect the different HNO_3 production pathways. However, when using the best known rates and N isotopic fractionation for this rection and testing different scenarios (i.e., 5%, 10% and 15% of total secondary HONO production), we can only explains the observed $\delta^{15}N$ results with less than 5% of daytime HONO production from nitrate photolysis. Consequently, based upon our $\delta^{15}N$ analysis, we did not incorporate this reaction for $\delta^{18}O$ analysis.

References:

Akagi, S. K., Craven, J. S., Taylor, J. W., McMeeking, G. R., Yokelson, R. J., Burling, I. R., Urbanski, S. P., Wold, C. E., Seinfeld, J. H., Coe, H., Alvarado, M. J., and Weise, D. R.: Evolution of trace gases and particles emitted by a chaparral fire in California, Atmos Chem Phys, 12, 1397–1421, https://doi.org/10.5194/acp-12-1397-2012, 2012.

Alvarado, M. J., Logan, J. A., Mao, J., Apel, E., Riemer, D., Blake, D., Cohen, R. C., Min, K.-E., Perring, A. E., Browne, E. C., Wooldridge, P. J., Diskin, G. S., Sachse, G. W., Fuelberg, H., Sessions, W. R., Harrigan, D. L., Huey, G., Liao, J., Case-Hanks, A., Jimenez, J. L., Cubison, M. J., Vay, S. A., Weinheimer, A. J., Knapp, D. J., Montzka, D. D., Flocke, F. M., Pollack, I. B., Wennberg, P. O., Kurten, A., Crounse, J., Clair, J. M. S., Wisthaler, A., Mikoviny, T., Yantosca, R. M., Carouge, C. C., and Le Sager, P.: Nitrogen oxides and PAN in plumes from boreal fires during ARCTAS-B and their impact on ozone: an integrated analysis of aircraft and satellite observations, Atmospheric Chem. Phys., 10, 9739–9760, https://doi.org/10.5194/acp-10-9739-2010, 2010.

Alvarado, M. J., Lonsdale, C. R., Yokelson, R. J., Akagi, S. K., Coe, H., Craven, J. S., Fischer, E. V., McMeeking, G. R., Seinfeld, J. H., Soni, T., Taylor, J. W., Weise, D. R., and Wold, C. E.: Investigating the links between ozone and organic aerosol chemistry in a biomass burning plume from a prescribed fire in California chaparral, Atmospheric Chem. Phys., 15, 6667–6688, https://doi.org/10.5194/acp-15-6667-2015, 2015.

Ammann, M., Kalberer, M., Jost, D. T., Tobler, L., Rössler, E., Piguet, D., Gäggeler, H. W., and Baltensperger, U.: Heterogeneous production of nitrous acid on soot in polluted air masses, Nature, 395, 157–160, https://doi.org/10.1038/25965, 1998.

Finlayson-Pitts, B. J., Wingen, L. M., Sumner, A. L., Syomin, D., and Ramazan, K. A.: The heterogeneous hydrolysis of NO2 in laboratory systems and in outdoor and indoor atmospheres: An integrated mechanism, Phys. Chem. Chem. Phys., 5, 223–242, https://doi.org/10.1039/B208564J, 2003.

Fischer, E. V., Jaffe, D. A., Reidmiller, D. R., and Jaeglé, L.: Meteorological controls on observed peroxyacetyl nitrate at Mount Bachelor during the spring of 2008, J. Geophys. Res. Atmospheres, 115, https://doi.org/10.1029/2009JD012776, 2010.

George, C., Strekowski, R. S., Kleffmann, J., Stemmler, K., and Ammann, M.: Photoenhanced uptake of gaseous NO2 on solid organic compounds: a photochemical source of HONO?, Faraday Discuss., 130, 195–210, https://doi.org/10.1039/b417888m, 2005.

Kebede, M. A., Bish, D. L., Losovyj, Y., Engelhard, M. H., and Raff, J. D.: The Role of Iron-Bearing Minerals in NO2 to HONO Conversion on Soil Surfaces, Environ. Sci. Technol., 50, 8649–8660, https://doi.org/10.1021/acs.est.6b01915, 2016.

Liu, X., Zhang, Y., Huey, L. G., Yokelson, R. J., Wang, Y., Jimenez, J. L., Campuzano-Jost, P., Beyersdorf, A. J., Blake, D. R., Choi, Y., Clair, J. M. S., Crounse, J. D., Day, D. A., Diskin, G. S., Fried, A., Hall, S. R., Hanisco, T. F., King, L. E., Meinardi, S., Mikoviny, T., Palm, B. B., Peischl, J., Perring, A. E., Pollack, I. B., Ryerson, T. B., Sachse, G., Schwarz, J. P., Simpson, I. J., Tanner, D. J., Thornhill, K. L., Ullmann, K., Weber, R. J., Wennberg, P. O., Wisthaler, A., Wolfe, G. M., and Ziemba, L. D.: Agricultural fires in the southeastern U.S. during SEAC4RS: Emissions of trace gases and particles and evolution of ozone, reactive nitrogen, and organic aerosol, J. Geophys. Res. Atmospheres, 121, 7383–7414, https://doi.org/10.1002/2016JD025040, 2016.

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

Scharko, N. K., Martin, E. T., Losovyj, Y., Peters, D. G., and Raff, J. D.: Evidence for Quinone Redox Chemistry Mediating Daytime and Nighttime NO2-to-HONO Conversion on Soil Surfaces, Environ. Sci. Technol., 51, 9633–9643, https://doi.org/10.1021/acs.est.7b01363, 2017.

Stemmler, K., Ammann, M., Donders, C., Kleffmann, J., and George, C.: Photosensitized reduction of nitrogen dioxide on humic acid as a source of nitrous acid, Nature, 440, 195–198, https://doi.org/10.1038/nature04603, 2006.

Stockwell, C. E., Yokelson, R. J., Kreidenweis, S. M., Robinson, A. L., DeMott, P. J., Sullivan, R. C., Reardon, J., Ryan, K. C., Griffith, D. W. T., and Stevens, L.: Trace gas emissions from combustion of peat, crop residue, domestic biofuels, grasses, and other fuels: configuration and Fourier transform infrared (FTIR) component of the fourth Fire Lab at Missoula Experiment (FLAME-4), Atmospheric Chem. Phys., 14, 9727–9754, https://doi.org/10.5194/acp-14-9727-2014, 2014.

Talukdar, R. K., Burkholder, J. B., Schmoltner, A.-M., Roberts, J. M., Wilson, R. R., and Ravishankara, A. R.: Investigation of the loss processes for peroxyacetyl nitrate in the atmosphere: UV photolysis and reaction with OH, J. Geophys. Res. Atmospheres, 100, 14163–14173, https://doi.org/10.1029/95JD00545, 1995.

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

Yokelson, R. J., Crounse, J. D., DeCarlo, P. F., Karl, T., Urbanski, S., Atlas, E., Campos, T., Shinozuka, Y., Kapustin, V., Clarke, A. D., Weinheimer, A., Knapp, D. J., Montzka, D. D., Holloway, J., Weibring, P., Flocke, F., Zheng, W., Toohey, D., Wennberg, P. O., Wiedinmyer, C., Mauldin, L., Fried, A., Richter, D., Walega, J., Jimenez, J. L., Adachi, K., Buseck, P. R., Hall, S. R., and Shetter, R.: Emissions from biomass burning in the Yucatan, Atmos Chem Phys, 9, 5785–5812, https://doi.org/10.5194/acp-9-5785-2009, 2009.