

Comment on “Comment on “Isotopic evidence for dominant secondary production of HONO in near-ground wildfire plumes.””

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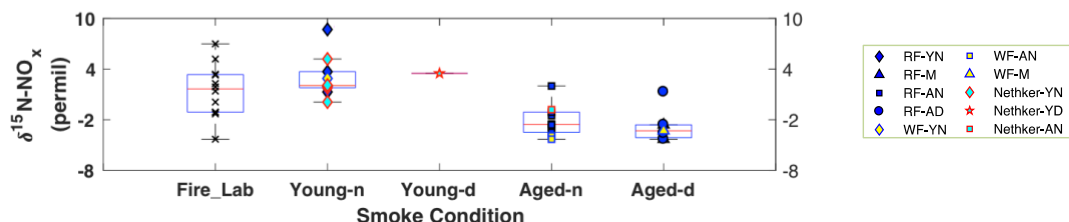
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We thank Dr. James Roberts for sharing his expertise on PAN. We acknowledge that at significant concentrations of PAN, i.e., comparable to that of NO_x in the atmosphere, and PAN could be efficiently collected in the permanganate impinger solution, it would interfere with the NO_x, also collected as nitrate, for isotopic analysis. It is uncertain whether significant PAN exists in the ground environments where we conducted our sampling, because no direct near-ground PAN concentration measurements in BB plume impacted areas are available. However, the isotopic results can shed unique light on whether PAN interference is important in our case. For aged smoke, we would expect $\delta^{15}\text{N-NO}_x$ to decrease from that in fresh emissions due to partial transformation of NO_x to additional oxidized N products (e.g. PAN), as well as isotopic exchange between NO_x and these oxidized species; both processes will leave ¹⁵N depleted in NO_x (relative to ¹⁴N) and ¹⁵N enrichment in PAN (Walters and Michalski, 2015). If PAN existed at significant concentrations that were 1) comparable with NO_x in the atmosphere, and 2) completely collected in the permanganate solution, then the $\delta^{15}\text{N-NO}_3^-$ would reflect the overall $\delta^{15}\text{N}$ of NO_x + PAN in the final reduced permanganate solution. In this case, we would expect that aged smoke would not shift from the $\delta^{15}\text{N-NO}_x$ range of young smoke, because $\delta^{15}\text{N}$ shifts in both PAN and NO_x could offset each other. However, our observed $\delta^{15}\text{N-NO}_x$ 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 ¹⁵N depletion in collected “NO_x” indicates the NO_x in 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). Therefore, we do not find significant isotopic evidence that PAN interferes with NO_x for $\delta^{15}\text{N}$ characterization in our study conditions.



Additionally, $\text{OH}+\text{NO}_2/\text{NO}+\text{RO}_2$ and NO_2+NO_3 are expected to slightly deplete ^{15}N in NO_x , due to their recombination reaction characteristics that have a secondary isotope effect. Our isotopic mass balance model was constructed to predict the $\delta^{15}\text{N}$ difference between NO_x and secondarily produced HONO. Within the timescale of HONO destruction (especially during the daytime), the $\delta^{15}\text{N}$ difference resulting from each of the HONO production reactions (4‰-40‰) is way larger than the change of $\delta^{15}\text{N}-\text{NO}_x$ itself (<0.3‰) resulting from either NO_2 -to-HONO conversion or $\text{OH}+\text{NO}_2/\text{NO}+\text{RO}_2$. As such, it is reasonable to consider that the change of $\delta^{15}\text{N}-\text{NO}_x$ itself has negligible impact on our modeling results.

In conclusion, our direct isotopic evidence does not show a significant PAN interference in the NO_x collected for isotopic analysis. However, it is interesting to see the contrast between our results and Dr. Roberts' expectation. As such, a direct PAN concentration measurement is really needed for future near-ground measurement of smoke plumes. In addition, a validated PAN collection method for isotopic analysis will also be helpful.

References:

Miller, D. J., Wojtal, P. K., Clark, S. C., and Hastings, M. G.: Vehicle NO_x 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.

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