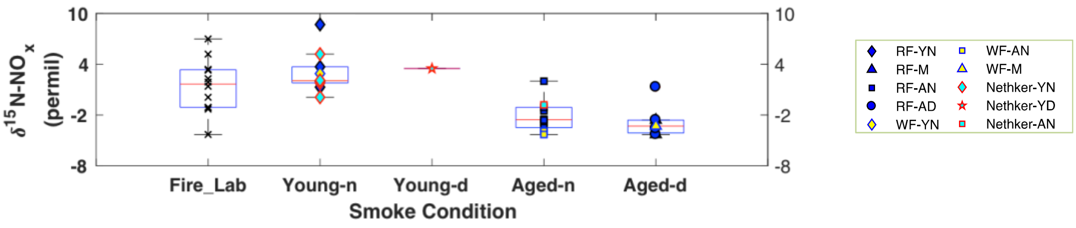
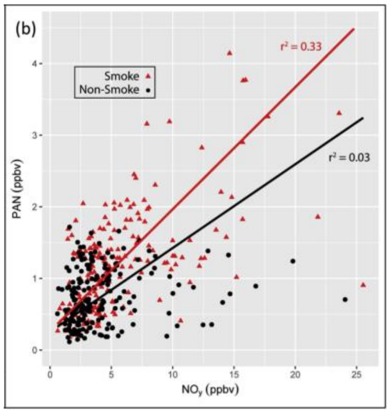
Dear Dr. Jaffe,

Thank you for your helpful comments on our paper!

Indeed, PAN can cause interference to the NO$_x$ in the alkaline collection system, if PAN exists in significant proportion relative to NO$_x$. However, as we pointed out in our response to Dr. Roberts' comments, our direct isotopic evidence does not show a significant PAN interference in the NO$_x$ collected for isotopic analysis. For aged smoke, we would expect $\delta^{15}$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 $^{15}$N depleted in NO$_x$ (relative to $^{14}$N) and $^{15}$N enrichment in PAN (Walters and Michalski, 2015). If PAN existed at significant concentrations that were 1) comparable with NO$_x$ in the atmosphere at the time, and 2) completely collected in the permanganate solution, then the $\delta^{15}$N-NO$_3^-$ would reflect the overall $\delta^{15}$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 $\delta^{15}$N-NO$_x$ range of young smoke, because $\delta^{15}$N shifts in both PAN and NO$_x$ could offset each other. However, our observed $\delta^{15}$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 $^{15}$N 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 $\delta^{15}$N characterization in our study conditions.



Most importantly, we appreciate you pointing out the ground measurement of PAN in Boise in 2017 by your group, which shows PAN of 1.22±0.72 ppbv for smoke days vs 0.74±0.39 ppbv for non-smoke days. We didn't reference it in our response to Dr. Roberts' comment because we thought there was no direct PAN measurement during our measurement period in the same environment for the same fire smokes and ages. In addition, we notice that in Figure 3 (b) (McClure and Jaffe, 2018), there are some overlaps of PAN/NO$_y$ between non-smoke and smoke periods. There are multiple times showing PAN/NO$_y$ < 0.1, with the extreme case of PAN/NO$_y$ < 0.04. As it has been pointed out in numerous publications from your group as well as others, fire emissions and the evolution of each species can have big heterogeneity depending on the fire conditions and meteorological conditions. Although PAN/NO$_y$ < 0.1is less probable, we could not rule out the possible conditions with low interference of PAN with NO$_x$.



Indeed, we agree that correction of NO$_x$ for PAN will yield more accurate NO$_x$ isotopic composition. This is something we have been actively pursuing (see below). However, it is impossible to accurately quantify the interference of PAN on NO$_x$ isotopic composition without simultaneous PAN concentration measurement, given the high temporal and spatial heterogeneity of both emissions and chemical evolution.

We believe that our work, as the first isotopic investigation of real-world wildfire derived reactive nitrogen, opens multiple channels for improvements via collaboration with other research groups including yours.

Particularly, we deem this helpful discussion as a unique opportunity and an effective way for us to improve the quantification of reactive nitrogen isotopic composition, interpretation of the isotopic results, and eventually the characterization of reactive nitrogen chemistry of not just wildfire smokes, but also other environments. A progressive approach has been designed and partially practiced:

1. In this summer's field study for quantifying the reactive nitrogen isotopic composition in an urban setting (Detroit, MI), in addition to deploying the collection system for offline isotopic analysis and a real-time $NO_x$ analyzer (chemiluminescence), we added another $NO_x$ analyzer connected with a HONO scrubber, and a real-time $NO_2$ analyzer (absorption spectroscopy). This allows us to quantify real-time [$NO_z$]-[HONO], which includes PAN, during each of our sampling periods.

2. We are developing a 0-D box model comprised of a nearly complete reactive nitrogen mechanism, with a set of comprehensive isotopic fractionation mechanisms based on kinetics and thermodynamics. This will allow for quantitative correction of the $NO_x$ collection technique for PAN under different product distribution scenarios.

3. Given your group's expertise in PAN measurement, we would be very interested to join in on future field measurements of (but not limited to) wildfire smokes. This will provide an essential opportunity to improve our $NO_x$ isotopic composition quantification, particularly in environments where PAN can be important.

We would like to reiterate we hope to benefit from the helpful discussion with you and Dr. Roberts as well as the entire atmospheric chemistry community. Thank you!

Regards,
Jiajue Chai

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