Dear Dr. Jaffe,

Thank you for your helpful comments on our paper!

Indeed, PAN can cause interference to the NOx in the alkaline collection system, if PAN exists in significant proportion relative to NOx. 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 NOx collected for isotopic analysis. For aged smoke, we would expect δ15N-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 15N depleted in NOx (relative to 14N) and 15N enrichment in PAN (Walters and Michalski, 2015). If PAN existed at significant concentrations that were 1) comparable with NOx in the atmosphere at the time, and 2) completely collected in the permanganate solution, then the δ15N-NOx would reflect the overall δ15N of NOx + PAN in the final reduced permanganate solution. In this case, we would expect that aged smoke would not shift from the δ15N-NOx range of young smoke, because δ15N shifts in both PAN and NOx could offset each other. However, our observed δ15N-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 15N depletion in collected "NOx" indicates the NOx 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 NOx for δ15N characterization in our study conditions.

![Box whisker plots for δ18O-HONO (a), δ15N-HONO (b) and δ15N-NOx (c).](image)

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 smoke and ages. In addition, we notice that in Figure 3 (b) (McClure and Jaffe, 2018), there are some overlaps of PAN/NOx between non-smoke and smoke periods. There are multiple times showing PAN/NOx < 0.1, with the extreme case of PAN/NOx < 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/NOx < 0.1 is less probable, we could not rule out the possible conditions with low interference of PAN with NOx.

Indeed, we agree that correction of NOx for PAN will yield more accurate NOx isotopic composition. This is something we have been actively pursuing (see below). However, it is impossible to accurately quantify the interference of PAN on NOx 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 NOx analyzer (chemiluminescence), we added another NOx analyzer connected with a HONO scrubber, and a real-time NO2 analyzer (absorption spectroscopy). This allows us to quantify real-time [NO2]-[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 NOx 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 NOx 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

References:

