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Comment on acp-2021-715

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Referee comment on "Comment on "Isotopic evidence for dominant secondary production of HONO in near-ground wildfire plumes" by Chai et al. (2021)" by James M. Roberts, Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-715-RC1, 2021

I think the issue raised by Roberts, regarding the paper by Chai et al 2021 are very real and important. PAN is well known to decompose in alkaline solutions. I also want to point out that Chai et al in their response to Roberts are wrong. We have made direct measurements of PAN at the surface in Boise Idaho. The concentrations of PAN we found during smoke events in this urban area are comparable to NOx. However this will depend a great deal on the mixing of smoke and surface temperatures.

Many studies have shown that PAN is a major component of NOy in smoke plumes. While this chemistry is not fully understand, it is absolutely clear that a large fraction of the NOx is sequestered as PAN, often very rapidly (see for example Alvarado et al. 2010; Baylon et al. 2015; Briggs et al. 2016; Juncosa et al 2021). The question of how and when this PAN reappears as NOx and contributes to O_3 formation was our primary motivation for a 2017 study in Boise Idaho, as reported by McClure and Jaffe (2018). We measured PAN in Boise in Aug-Sept 2017 when there were substantial smoke plumes in the region. We reported daytime means for smoky days of PAN=1.2 ppb, NO=1.0 ppb, NOy = 5.8 ppb. Concentrations were lower on non-smoky days. NO_2 was not measured, but we can estimate it from the NO data to be ca 1-2 ppb.

This is for an urban area, where a significant fraction of NOx is associated with nearby traffic emissions. For this location, we can estimate then that PAN was about 50% of the NOx concentrations. I would expect that in a more rural or remote location, PAN could equal or exceed NOx. I would also note that for this time period, the mean daily max temp in Boise was 29.8^{o}C, which will drive the PAN decomposition from even higher PAN/NOy ratios in smoke plumes.

So what does all this mean for the analysis of Chai? Its not clear if the data could be corrected for this without PAN measurements, but it seems the should try. In my opinion, a method that has a significant PAN interference can not be used to study the isotopic composition of NOx in wildfire smoke.

Refs:

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