

Review of ACP 2021-225, Isotopic Constraints on Wildfire derived HONO, by Chai, et al.,

This paper presents ^{15}N and ^{18}O isotopic analyses of HONO and NO_x in ground-based samples impacted by wildfire smoke. Unfortunately, it is clear from extensive previous work (Grosjean et al., 1984, Grosjean and Harrison, 1985, and references in Roberts 1990) that the method for sampling NO_x has a 1:1 interference from PAN compounds. This renders the NO_x measurements reported here invalid since we know that PAN and associated compounds are significant N products in even relatively ‘young’ wildfire plumes. There might still be information in these measurements that could be a useful addition to our understanding of HONO chemistry in these plumes, but the over-all analysis will need to be completely re-thought. In addition to the above, I found the presentation very difficult to follow, and some sections having to do with HONO alone will need to be extensively revised for the paper to be acceptable. This paper is simply not valid in its current form due to the problem with NO_x measurement, and must be rejected for publication at this time. I have the following General Comments that would also need to be addressed, in any future publication, but have refrained from making specific comments.

General Comments

The collection and hydrolysis of PAN in alkaline solution was an early method for the calibration of PAN standards (see for example Stephens, 1969, Grosjean et al., 1984, Grosjean and Harrison, 1985, and references in Roberts 1990) but has somewhat fallen out of favor with the advent of efficient photochemical sources for PANs. The method used for NO_x collection in this paper uses the same conditions (e.g. [OH⁻] concentrations) as those PAN collection techniques. Moreover, the alkaline hydrolysis of PANs produces nitrite ion, which will be oxidized by the KMnO₄ in the impinger solution in the same manner as the nitrite that arises from NO_x collection. Therefore, we can conclude with considerable confidence that PANs will interfere completely with the NO_x method used in this work.

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 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.

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

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 $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ for O₃ relative to H₂O? but both reactions 6 and 7 involve NO₂ and (which gets an ^{18}O effect from O₃). This whole phenomenon is just not well explained

at all in Appendix B. Also, the nomenclature in Appendix B 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?

Nighttime processing of NO_x through NO_3 and N_2O_5 can be quite important chemical pathways to HNO_3 . Wouldn't these impart an even large $\delta^{18}O$ 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.

References

Grosjean, D., Fung, K., Collins, J., Harrison, J., and Breitung, E., Portable generator for on-site calibration of peroxyacetyl nitrate analyzers, *Anal. Chem.*, 56, 569-573, 1984.

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