

Interactive comment on “Alkyl nitrates in the boreal forest: Formation via the NO₃, OH and O₃ induced oxidation of BVOCs and ambient lifetimes” by Jonathan Liebmann et al.

Anonymous Referee #1

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Review of Liebmann et al., 2019: “Alkyl nitrates in the boreal forest: Formation via the NO₃, OH, and O₃ induced oxidation of BVOCs and ambient lifetimes”

This manuscript uses measurements from a boreal forest to compare the relative importance of alkyl nitrate formation via NO₃, O₃, and OH oxidation pathways during both day and night. They find, somewhat surprisingly, that NO₃ oxidation of BVOCs accounts for up to half the daytime production of alkyl nitrates, and that there are approximately equal rates of alkyl nitrate production during day and during night. Additionally, the authors calculate a relatively short steady-state alkyl nitrate lifetime of 2 hours, implying that heterogeneous hydrolysis is likely an important loss process in this

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environment.

These are interesting results on the fractional contribution of different oxidation pathways to alkyl nitrate production and on the lifetime of alkyl nitrates in a boreal forest. The paper is well organized and does a nice job accounting for the uncertainties in various calculations. I recommend publication.

Some questions and comments to improve the manuscript can be found below.

Major comments: 1. Some parts of the manuscript would benefit from being more quantitative. For example, on page 5, line 14 (and similarly on page 7, line 1), the authors state that “only the handful of biogenic VOCs listed contributed significantly.” More quantification (i.e., biogenic VOCs contributed to $>x\%$ of the observed reactivity) would be helpful. Additionally, (page 10, line 6), please be quantitative and specify the aerosol surface area measured, instead of discussing it in purely relative terms.

2. It would be helpful if the authors were able to observationally constrain some of the numbers they estimate in the manuscript. For example, on page 5, line 26 the authors assign an alkyl nitrate yield of 0.7 to unattributed VOCs because they suspect the missing reactivity is from highly reactive BVOCs with high yields. Could this number be observationally constrained using the quantified missing reactivity and the ANs production rate? Likewise, is it possible to get an observational constraint on the alkyl nitrate deposition velocity (page 9, line 29)? Or at least compare the HNO_3 production implied by the estimated hydrolysis rates to observed increases in aerosol inorganic nitrate? And lastly (page 10), can you use the aerosol surface area that was measured to estimate an aerosol uptake efficiency for alkyl nitrates, rather than simply saying the “efficiency could be >0.1 ”?

3. I am curious how much the seasonal changes over the course of the IBairn study affected the various production and loss processes for alkyl nitrates. Do averages from the first half of the study (summer) and the second half of the study (autumn) give significantly different results, or are there minimal differences?

4. Is it possible to connect the individual alkyl nitrates observed by CIMS to the ANs production rates of alkyl nitrates calculated from individual VOCs? Could this give any indication as to which VOCs contribute to the missing reactivity?

Minor comments: 1. Page 2, line 12: Why is reaction with O₃ only relevant in the boreal forest? 2. Page 2, line 30: Clarify to say "...the branching ratio to AN formation via NO₃ oxidation is generally..." 3. Equation 4: Typo—should include k₅ rather than k₃. 4. Page 6: Should RO₂ loss via reaction with NO₂ to form PANs also be accounted for? Or is it insignificant? 5. Page 8, line 8: Clarify to say that the ANs production from ozonolysis has a daytime minimum at noon (since the absolute minimum is really at night). 6. Figures 2 and 3: x-axis labels are confusing. 7. Page 9, line 15: I think your estimate uses the "steady-state" approximation rather than the "stationary-state" approximation. 8. Figure 6: Please define what your error bars are (standard deviation?). Additionally, the ends of some of the error bars are not visible in the plot. Is the fit you are doing to all points or only the average points that are plotted? What kind of fit are you using (OLS, RMA, York?)? 9. Page 9, line 25: Some alkyl nitrates (e.g., isoprene hydroxy nitrate) can be oxidized by OH with reasonable efficiency, and highly oxidized or carbonyl nitrates can be rapidly photolyzed (see Muller et al., 2014 and Xiong et al., 2016). Are these not relevant during IBAIRN? 10. Page 9, line 32: Should be "assessed" instead of "accessed." 11. Page 10, line 3: Was the calculation of average thermal velocity done at STP or at the average temperature and pressure during the campaign? Please specify. 12. Page 10, line 11: Consider citing Romer et al., 2016 and Zare et al., 2018 which also discuss ANs lifetimes and heterogeneous hydrolysis as a loss pathway for ANs. 13. A separate conclusion section would be helpful to the reader (i.e. add a section header before the last two paragraphs).

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