

## ***Interactive comment on “Direct measurement of NO<sub>3</sub> reactivity in a boreal forest” by Jonathan Liebmann et al.***

**Anonymous Referee #1**

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General Comments:

This paper presents first measurements of NO<sub>3</sub> reactivity in a biogenic VOC rich environment using a recently developed technique. The paper presents new results, is well written, and presents a thorough and straightforward analysis. Results for NO<sub>3</sub> reactivity should nicely complement those for OH reactivity, which have become a standard measurement for understanding photochemistry, especially in high biogenic emitting regions. The measurement of NO<sub>3</sub> reactivity provides a similar metric for nighttime oxidation, as well as new understanding of oxidation potential for NO<sub>3</sub> radicals during daytime. The novelty of this result will make this paper of high interest to the audience of ACP.

The only general comment is that this measurement may pertain to a boreal forest,

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but it is the first measurement of NO<sub>3</sub> in any environment. The authors may wish to consider broadening the title somewhat to at least encompass “high biogenic emitting regions”, since the results are new enough that they may generalizable beyond just a boreal forest.

Otherwise, the authors should respond to the following set of relatively minor comments.

Specific Comments:

Page 2, line 9: check grammar

Page 2, line 26: You may want to be more specific in your definition of terpenoids, which presumably include isoprene, monoterpenes and sesquiterpenes?

Page 6, line 11: calculated to be 14%, or calculated at 14%.

Page 7, line 20: Uncertainty in kOTG difficult to discern, as are values for kOTG on the linear scale given in figure 2. A log scale may be more effective for presentation.

Page 7, lines 27-30: The cited literature is generally not for forested areas. A better comparison would be to a paper such as Golz et al. (2001) or Ayres et al. (2016), which report unmeasurable NO<sub>3</sub> in heavily forested areas.

Gölz, C., J. Senzig, and U. Platt (2001), NO<sub>3</sub>-initiated oxidation of biogenic hydrocarbons, *Chemosphere - Global Change Science*, 3(3), 339-352, 10.1016/s1465-9972(01)00015-0.

Ayres, B. R., H. M. Allen, D. C. Draper, S. S. Brown, R. J. Wild, J. L. Jimenez, D. A. Day, P. Campuzano-Jost, W. Hu, J. de Gouw, A. Koss, R. C. Cohen, K. C. Duffey, P. Romer, K. Baumann, E. Edgerton, S. Takahama, J. A. Thornton, B. H. Lee, F. D. Lopez-Hilfiker, C. Mohr, P. O. Wennberg, T. B. Nguyen, A. Teng, A. H. Goldstein, K. Olson, and J. L. Fry (2015), Organic nitrate aerosol formation via NO<sub>3</sub> + biogenic volatile organic compounds in the southeastern United States, *Atmos. Chem. Phys.*, 15(23), 13377-

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13392, 10.5194/acp-15-13377-2015.

Page 8, line 6: The effect of lower wind speeds is easily tested. Were reactive VOCs also greater during these periods?

Page 8, line 12, and Figure 4 caption. "Expanded view" is a less colloquial expression than "zoom in". Minor suggestion, at authors discretion.

Page 11, line 12 and Figure 7: How well correlated are the measured and calculated NO<sub>3</sub> reactivities? A scatter plot and linear fit, possibly separated into type 1 and 2 events, would be instructive.

Page 12, line 1: Define what is meant by "statistically significant" here. Based on correlation or based on error analysis in the time series.

Page 13, lines 10-11: Have the authors considered reaction of NO<sub>3</sub> with HO<sub>2</sub> or RO<sub>2</sub>? How well does the NO<sub>3</sub> reactivity instrument measure radical-radical reactions such as this, and could they contribute significantly to NO<sub>3</sub> reactivity in these environments where NO<sub>3</sub> reactivity is large?

Page 13, line 16, equation 3: Loss of NO<sub>3</sub> through either direct heterogeneous uptake or through N<sub>2</sub>O<sub>5</sub> heterogeneous uptake is not included. This is very likely appropriate since these processes are probably slow compared to NO reaction, photolysis and VOC reaction for NO<sub>3</sub> at the SMEAR site. This should at least be mentioned.

Page 15, line 23-27: The diel cycle in the fraction of NO<sub>3</sub> reacting with VOCs is a quite useful metric and shows the relevance of NO<sub>3</sub> as a daytime oxidant. However, the NO<sub>3</sub> production rate is itself quite small at this location. Can the inferred absolute oxidation rate also be given (i.e., NO<sub>3</sub> production  $\times$   $f$ ), and can this also be compared to similar estimates for OH or O<sub>3</sub> oxidation during the day?

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Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-975>, 2017.