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Interactive comment on "Day- and Night-time Formation of Organic Nitrates at a Forested Mountain-site in South West Germany" *by* Nicolas Sobanski et al.

Anonymous Referee #1

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Sobanski et al. present analysis of the measurements of organic nitrates from two field deployments at the Taunus Observatory in Germany. This analysis is a useful contribution to our understanding of the role of organic nitrates in the NOx budget on a global scale, and raises interesting questions about the relative fate of organic nitrates during the day and night. I would suggest publication after the following comments are addressed.

General Comments:

1. When calculating average production rates of alkyl nitrates during day and night, the authors use campaign average values for each term. Given the variety of conditions sampled during the campaign, it seems possible that using campaign averages will bias

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the results (if, for example, the mixture of VOCs and therefore the alkyl nitrate yield is different on nights with higher concentrations of NO_2 and O_3). The use of campaign average values in calculations should either be avoided or the consequences of them discussed.

2. The discussion of the differences in alkyl nitrate yield between PARADE and NOTOMO should be expanded further. While the proposed explanation, that BVOC emissions were lower during NOTOMO, is plausible, I would appreciate further discussion of alternative explanations for the observations. In particular, the authors should consider the possibility that the NOTOMO observations of O_3 and ANs represent a highly aged airmass where the assumptions required for Eq. 6 do not apply.

Specific Comments:

Page 1, Line 26-27: Since HNO_3 does not appreciably return NO_x to the atmosphere, it is incorrect to describe NO_x as being temporarily sequestered as HNO_3.

Page 3, Line 3: NO_y should be defined in this manuscript.

Page 3, Line 10: The abbreviation TD-CRDS should be defined here, the first time it is used, rather than on page 4.

Page 4, Section 3.1: Is the TD-CRDS measurement of ANs gas-phase only? Given the potential importance of particle-phase chemistry to understanding the nighttime concentration of ANs, the response of the TD-CRDS instrument to particulate organic nitrates should be discussed in this section.

Page 5, Line 25: Was $J(NO_2)$ measured directly, or was it modeled?

Page 9, Line 22: Given that direct measurements of NO_3 are available for this campaign, why are those measurements not used to calculate the nighttime alkyl nitrate production rate?

Page 9, Line 24 and Line 29: Which days were included when calculating mean nighttime mixing ratios? All days, only days including in Fig. 6, or some other combination?

Page 9, Line 25: A citation for these alkyl nitrate yields should be given.

Page 9, Line 27-28: Some justification for assuming that heterogeneous N2O5 loss is minimal should be included.

Page 9, Equation 2: See general comment 1.

Page 10, Line 5: What uncertainty in the calculated value of OH does this correlation introduce?

Page 10, Line 6-7: Is the campaign mean calculated for all days or for only times included in Fig. 6?

Page 10, Line 10, Equation 3: See general comment 1.

Page 10, Line 20: I typically think of deposition dropping to near zero at night, since turbulent mixing is low. The authors should discuss further the likelihood of enhanced nighttime deposition.

Page 10, Line 23-24: Can the SOA yields reported by Fry et al. 2011, 2014 be used to estimate the fraction of ANs produced that are likely to remain in the gas phase, and can that fraction be used to adjust Eq. 2 to describe only the gas-phase production of alkyl nitrates?

Page 11, Equation 5: The concentration of ozone and ANs should include the effect of chemical loss.

Page 12, Line 3-7: Under the conditions of the NOTOMO campaign, what uncertainty in AN concentration does the correction procedure introduce?

Page 12, Line 20-22: This is likely an overestimate of the range of isoprene alkyl nitrate yield. Recent work on the isoprene branching ratio has generally found branching ratios on the higher end of this range (9-15%) (Teng et al., 2015, Xiong et al., 2015)

Page 12, Line 33: Photolysis and chemical loss of alkyl nitrates is often a more important loss process than deposition (Xiong et al., 2015).

Page 13, Line 6-9: Any explanation for the low concentrations of alkyl nitrates should also be able to explain the high concentration of ozone encountered during the NOTOMO campaign.

Page 13 Line 7: Given that on average, NOTOMO was warmer and sunnier than PARADE (page 8), what magnitude of changes in VOC emissions is expected between the two campaigns? Is this change large enough to explain the low observed yield of alkyl nitrates?

Page 13 Line 8: Based on the mixture of non-biogenic VOCs measured during PARADE, would decreased concentrations of BVOCs lead to a lower average value of alpha? Is this value low enough to explain the observed O3-AN slope during NOTOMO?

Page 18, Line 20, Table 1: Several of the values in this table disagree with those listed in Perring et al, 2013, the listed source for the yield. This includes i-pentane(0.35/0.07), isoprene (0.044/0.07) and i-butane(0.255/0.096). The values in Table 1 should either be updated or new references given.

Technical Corrections:

Page 1 Line 12: "Futher" should be "Further"

Page 6, Line 15: Extra period after Fig. 2.

Page 11, Line 14 Equation 4: There are some mis-matched parentheses in this equation

Page 18, Table 1: The mean noon time mixing ratio unit appears to be pptv, and not ppbv as written

Additional References:

Xiong, F., McAvey, K. M., Pratt, K. A., Groff, C. J., Hostetler, M. A., Lipton, M. A., Starn, T. K., Seeley, J. V., Bertman, S. B., Teng, A. P., Crounse, J. D., Nguyen, T. B., Wennberg, P. O., Misztal, P. K., Goldstein, A. H., Guenther, A. B., Koss, A. R., Olson, K. F., de Gouw, J. A., Baumann, K., Edgerton, E. S., Feiner, P. A., Zhang, L., Miller, D. O., Brune, W. H., and Shepson, P. B.: Observation of isoprene hydroxynitrates in the southeastern United States and implications for the fate of NOx, Atmos. Chem. Phys., 15, 11257-11272, doi:10.5194/acp-15-11257-2015, 2015.

Teng, A. P., Crounse, J. D., Lee, L., St. Clair, J. M., Cohen, R. C., and Wennberg, P. O.: Hydroxy nitrate production in the OH-initiated oxidation of alkenes, Atmos. Chem. Phys., 15, 4297-4316, doi:10.5194/acp-15-4297-2015, 2015.

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