Reply to Referee #2

We thank Referee #2 for the manuscript comments, which we have responded to below.

Interactive comment on "Contributions of individual reactive biogenic volatile organic compounds to organic nitrates above a mixed forest" by K. A. Pratt et al.

Anonymous Referee #2

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Pratt et al. use a 1-D chemistry model to describe the atmospheric chemistry above a broadleaf forest, focusing on organic nitrate formation. Overall, the paper is clear and well-written. In addition to points raised by the first reviewer, I have three concerns that the authors should consider prior to publication in ACP. Aside from the model description, the paper introduces little new science aside from the suggestion that as forest succession occurs, organic nitrates are derived from monoterpenes rather than isoprene. I think this does not provide adequate motivation for the paper, and suggest that the authors carefully frame their results in terms of the impact of their modeled organic nitrates on NOx reservoirs, ozone formation, or potential for SOA formation. This would greatly strengthen the Discussion section of the paper, and provide more context for the study.

> *We disagree with the assertion that the paper introduces little new science. In particular, as noted by Referee #1, a significant aspect of this study that warrants attention is the predicted importance of daytime* NO_3*-isoprene chemistry, as well as* NO_3 *chemistry in general. The previously supplemental figure showing simulated primary isoprene nitrate production from* NO_3 *chemistry has been moved to the main text, and the manuscript has been revised to place more emphasis on this point. Also, to place additional emphasis on the organic nitrate conclusions, the section regarding OH reactivity has been removed from the manuscript, as suggested by Referee #1. Another significant, unique aspect of this study is that 57 individual BVOCs were examined, highlighting the most important reaction rate constants and yields that must be examined in future laboratory studies to further our understanding of* $RONO_2$ *chemistry and fates.*

My other concern regards the lack of measurement-model comparison of organic nitrates. The authors describe measurements of RONO2 in the Measurements section (p.17037, l.16), but do not compare the observations to the model. This would be a worthwhile and extremely useful figure that would provide insight into the ability of the model to replicate the data.

> *A discussion of measured and modeled* $RONO_2$ *was previously given on pages 17050 and 17054. We agree that this is an important aspect of our study. Thus, we have added a figure showing the measured and modeled diurnal cycles of the two most abundant isomeric isoprene nitrates, as discussed in the response to Referee #1. Thank you for this input!*

Similarly, I am surprised that the authors don't compare observed and modeled NO and NO2 - this would be a good test of the model.

> *As stated in the original manuscript (p.17044), NO and NO_2 were not calculated within the model. Rather, measured NO concentrations were used to calculate the term β, which describes the fraction of time RO_2 reacts with NO versus HO_2 and RO_2.*

p.17046, l. 15-16. Please explain the discrepancy in Vdep between '1st-generation isoprene oxidation products'(0.5 cm/s) and 'secondary organic nitrates' (2.5 cm/s). Considering the uncertainty in these values, the authors should discuss/identify how sensitive the model is to making these both 0.5 or 2.5 cm/s.

> *Zhang et al. (2003) predicted deposition velocities of 0.3-0.7 cm/s for MVK and MACR for deciduous needleleaf trees, deciduous broadleaf trees, and mixed wood forests. Thus, we assumed the value of 0.5 cm/s for first-generation isoprene oxidation products, including MVK, MACR, and C_5-unsaturated hydroxyaldehyde isomers. For organic nitrates, Zhang et al. (2003) predicted higher deposition velocities of 0.7-1.0 cm/s for organic nitrates. Also, as noted in the text, Farmer and Cohen (2008) calculated a deposition velocity of 2.7 cm/s for $RONO_2$ at a pine forest. Thus, higher deposition velocities of 1.5 and 2.5 cm/s were assumed for primary and secondary organic nitrates. Indeed, there is significant uncertainty regarding the deposition velocities of oxidation products. As suggested, two sensitivity model runs were performed using either 0.5 cm/s or 2.5 cm/s for the deposition velocities of all oxidation products. Using a deposition velocity of 0.5 cm/s, [$RONO_2$] increased by 28%. In contrast, a deposition velocity of 2.5 cm/s resulted in decreased [$RONO_2$] by 11% and, in particular, [MVK+MACR] by 32%. The results of this sensitivity test are now discussed in the manuscript.*

Note that all of my technical corrections were identified by the first reviewer, so I will not replicate the list.

Response References:

Farmer, D. K., and Cohen, R. C.: Observations of HNO_3, ΣAN, ΣPN, and NO_2 fluxes: evidence for rapid HO_x chemistry within a pine forest canopy, Atmos. Chem. Phys., 8, 3899-3917, 2008.

Zhang, L., Brook, J. R., and Vet, R.: A revised parameterization for gaseous dry deposition in air-quality models, Atmos. Chem. Phys., 3, 2067-2082, 2003.