

We thank two reviewers for their positive and constructive comments. Our responses to the comments are provided below. The reviewers' comments are in bold, our responses in normal text, and changes made to the manuscript are shown in red italics block quotes. Page and line numbers refer to the first submission.

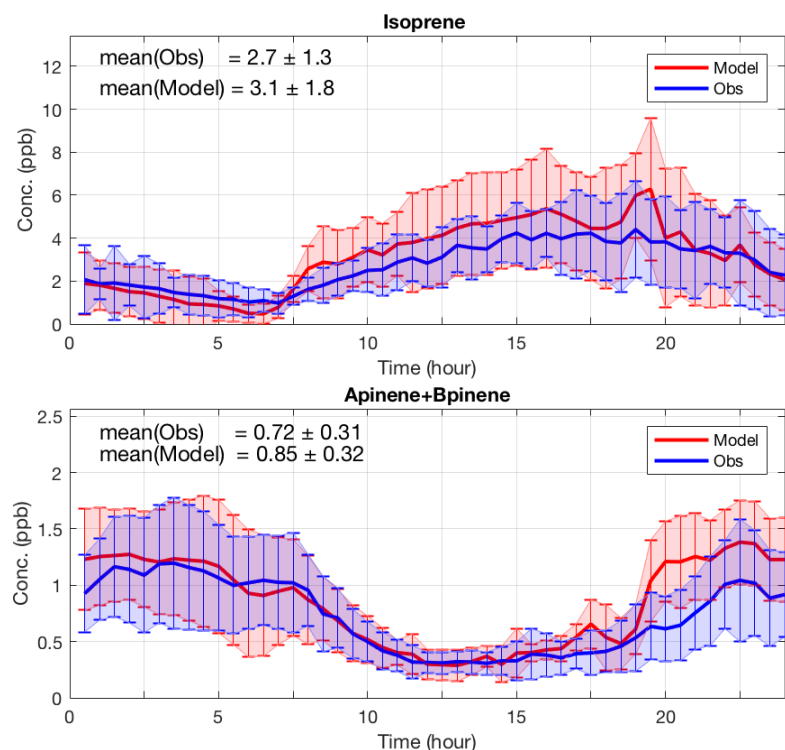
## Response to Referee #2

**This is a nice paper that looks into details of organic nitrate chemistry, with recent new understanding on this topic. The authors develop a new mechanism in WRF-Chem model and compare model simulations to observations in Southeast US during SOAS 2013. They find that their model is generally in good agreement with observations, assuming organic nitrates is short lived with a lifetime of 2-3h. The paper is well written. I would recommend publication on ACP after the following comments are addressed:**

**1. As organic nitrates are largely driven by biogenic VOCs, it is important for authors to evaluate isoprene and monoterpene concentrations in their model. Isoprene and monoterpene measurements have been shown in Fisher et al. [2016]. I assume that they are available for comparison.**

We have added the requested figure to the Supplement and described it in the text as:

*Page 12, 6 “In Fig S5, we also provide additional model evaluation for isoprene and monoterpene concentrations.”*



*“Figure S4: Median diurnal cycles of observed and simulated CH<sub>2</sub>O, isoprene and monoterpenes at Centreville during the 2013 SOAS campaign. The vertical bars show the interquartile range of the hourly data. The panel includes mean of the simulated and observed values.”*

**2. The authors have done a detailed comparison with Fisher et al. [2016]. It is important to point out that Fisher et al. [2016] assumes a 9% yield for first generation isoprene nitrates, while it is assumed 11.7% in this paper. Given the higher yield and slower aerosol hydrolysis in this study, could authors comment on why these two studies show similar amount of total organic nitrates in their models?**

Our predicted RONO<sub>2</sub> concentrations are within the observed variability but we have estimated the mean of total RONO<sub>2</sub> (~260 ppt) to be higher than the value (~200 ppt) reported in Fisher et al. (2016). This difference is not too dissimilar from the difference in yields. In addition, the higher yield in the mechanism in our paper is balanced by more rapid deposition of second-generation monoterpene nitrates (following Browne et al., 2014) than in Fisher et al. (2016).

**3. The authors appear to have ignored another model study on this topic, Li et al. [2018]. It seems that Li et al. [2018] also did a detailed analysis on first- and second generation isoprene nitrates using data collected in Southeast US. It might be worthwhile to compare this model to their results in details.**

Thanks to the reviewer for pointing out this oversight. Key differences are summarized in the following table and we have added a discussion comparing our results to Li et al. (2018) to the paper as follows.

	This study	Li et al. (2018)
Model	Chemical transport WRF-Chem v3.5 model	AM3 global chemistry–climate model
Horizontal Resolution	12 km	50 km
Isoprene nitrate yield	11.7% (yield of $\beta$ vs. $\delta$ isomers are 10.5% and 1.2% respectively)	10% (only $\beta$ isomer)
Isoprene NO <sub>3</sub> chemistry	Following Schwantes et al. (2015)	Based on the Leeds Master Chemical Mechanism (MCM v3.2)
Monoterpenes nitrate yield from OH chemistry	18% for low-reactivity monoterpenes and 22% for high-reactivity monoterpenes (following Browne et al., 2014)	Simplified monoterpenes nitrate chemistry with an organic nitrate yield 26% for one lumped monoterpenes
Monoterpenes nitrate yield from NO <sub>3</sub> chemistry	10% for low-reactivity monoterpenes and 70% for high-reactivity monoterpenes (following Browne et al., 2014)	10% for one lumped monoterpenes
Hydrolysis of RONO <sub>2</sub>	hydrolysis of gas-phase tertiary	2-step hydrolysis scheme:

	organic nitrates (hydrolysis lifetime = 3 hr)	heterogeneous uptake of organic nitrates onto aerosols and then hydrolysis of aerosol-phase nitrates (hydrolysis lifetime = 3 hr). In base case, only ISOPNB is assumed to hydrolyze.
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Page 9, 1-3 "Temporal variability in the total organic nitrates is reproduced with little bias ( $r^2=0.8$  and normalized mean bias (NMB) =32%). Although the mean of the simulated organic nitrates ( $0.26\pm 0.19$ ) slightly overestimates the mean of the observations ( $0.20\pm 0.1$ ), the medians are within the variability of the observations. *The simulated mean of total RONO<sub>2</sub> in this study is in the range of two other recent modeling studies over the Southeastern US in summer 2013 that simulated 200 ppt (Fisher et al., 2016) and 270 ppt (Li et al, 2018). However, in both of these studies RONO<sub>2</sub> derived from anthropogenic VOC precursors were not included. In our simulation, these organic nitrates represent ~20% of total RONO<sub>2</sub>. Specific sources of the differences include, the slightly smaller yield of 10% yield for isoprene nitrates and application of a 3 hr hydrolysis lifetime only for ISOPNB in Li et al., (2018). Fisher et al. (2016) apply a faster hydrolysis rate (1hr) for all organic nitrates and a lower yield (9% for isoprene nitrates).*"

Page 9, 4-8 "Inclusion of hydrolysis as a possible fate for tertiary organic nitrates results in significant improvement of the simulations compared to the observations (not shown here). Tertiary nitrates have shorter lifetime against hydrolysis under atmospheric conditions, compared to the lifetime against deposition (Fig. S1 in the Supplement) making them the most important sink of nitrates. *Li et al. (2018) also showed, by introducing the hydrolysis of ISOPNB, the model relative bias of total RONO<sub>2</sub> was reduced 18% during ICARTT (summer 2004) over the Southeastern United States.*"

Page 10, 31 "Among monoterpene nitrates, NO<sub>3</sub>-initiated nitrates (Ayres et al., 2015) and functionalized nitrates (Lee et al., 2016) have been shown to be an especially significant fraction of the total particle organic nitrate source at SOAS site. These findings imply that the remainder of the measured particle organic nitrates can be attributed to mono- or sesquiterpene derived RONO<sub>2</sub> including NO<sub>3</sub>-initiated terpene hydroxynitrates, terpene nitrooxyhydroperoxides and multifunctional terpene nitrates, which are simulated and present in the gas phase in our mechanism. If we interpret the aerosol nitrates to be these compounds, then we find a rough correspondence between the model and observations (see Fig. 5a and b). *However, Li et al. (2018) estimated a smaller contribution of gas-phase NO<sub>3</sub>-initiated monoterpene nitrates to total RONO<sub>2</sub> due to a lower molar yield (10% vs 70% for high-reactivity monoterpenes and 10% for low-reactivity monoterpenes in this study). In contrast, due to other differences in the mechanism they found a larger contribution of OH-initiated monoterpene nitrates to total RONO<sub>2</sub> than our finding in this study.*"

Page 13,13-15 "GEOS-Chem simulations by Fisher et al. (2016) reported a similar short lifetime by assuming a hydrolysis lifetime of 1 h lifetime for all tertiary and non-tertiary nitrates and not including the longer-lived small alkyl nitrates. *However, Li et al., (2018) estimated longer lifetimes for individual nitrates except ISOPNB, which they assumed to be hydrolyzed.*

**4. I would suggest that the authors include two review papers on this topic in the Introduction part, Carlton et al. [2018] and Mao et al. [2018].**

We add these references to the introduction and result sections.

*Page 1, 26-29 “ The oxidative chemistry of BVOCs affects the distribution of oxidants (OH, O<sub>3</sub> , NO<sub>3</sub> ) and the lifetime of NO<sub>x</sub> (=NO+NO<sub>2</sub> ), creating a feedback loop that affects oxidant concentrations, the lifetime of BVOCs and secondary organic aerosol formation (Carlton et al., 2018; Mao et al., 2018).”*

*Page 8, 16-18 “We evaluate our mechanism by comparison to SOAS observations in Bibb County, Alabama (32.90° N latitude, 87.25° W longitude) in summer 2013 (Carlton et al., 2018; Mao et al., 2018).”*

**5. It might be useful to mention vertical resolution of WRF-Chem, to help reader understand how well the model is representing nighttime boundary layer emission and chemistry.**

This comment was in common with Reviewer 1’s comment. We have added this information at the text as:

*Page 3, 26-30 “We use WRF-Chem version 3.5.1 (Grell et al., 2005) with a horizontal resolution of 12 km ~~and 30 vertical layers~~ over the eastern United States. Our simulation domain is defined on the Lambert projection, which is centered at 35°N, 87°W and has 290 and 200 grid points in the west–east and south–north directions, respectively (see Fig. 3 for the horizontal domain). **The vertical coordinate is hybrid sigma-pressure that covers 30 levels from the surface to 100 hPa. Near surface levels follow terrain and gradually transitions to constant pressure at higher levels. Vertical grid spacing varies with height such that finer spacing is assigned to the lower atmosphere while coarser vertical spacing is applied at higher levels. In this analysis, the model predictions are averaged over two lowest model levels used for comparison with ground-based measurements taken from a 20 m walk-up tower. The predicted concentrations in boundary layer are described as an average over 8 vertical model levels with a height that is comparable with the planetary boundary layer depth at midday at Southeastern United States in June 2013.**”*

**6. Page 10, Line 25, “They showed total particle organic nitrates have a dominant contribution from highly functionalized isoprene nitrates containing between six and eight oxygen atoms.” Is this correct about the isoprene nitrates dominating particle organic nitrates? If not, then this should not be the reason for “the difference between the modeled and observed contribution of isoprene nitrates to total organic nitrates”.**

Lee et al., (2016) have shown that “Each carbon number group in the particle phase exhibits a bell-shaped distribution, with the dominant contribution from ON typically comprising between six and eight oxygen atoms”. And we have found that “The largest difference between the modeled and observed contribution of isoprene nitrates to total organic nitrates is due to the modeled gas-phase multifunctional isoprene nitrates and isoprene nitrooxy hydroperoxides.” Accordingly, we have concluded that part of modeled gas-phase multifunctional isoprene nitrates can correspond with the part of observed particle organic nitrates. We have revised text as follows:

Page 10, 24-28 “They are simulated in the gas phase using RACM2\_Berkeley2 but we might interpret them as contributing to particle phase organic nitrate. That is consistent with the Lee et al. (2016) finding from observations of speciated particle organic nitrates during the SOAS campaign. They showed ~~total~~ particle ~~organic~~ isoprene nitrates have a dominant contribution from highly functionalized isoprene nitrates containing between six and eight oxygen atoms.”