

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 #1

Zare et al. present a description of an updated chemical mechanism for organic nitrate chemistry, focusing on isoprene and monoterpene nitrates. They apply the mechanism to the SOAS campaign over the US Southeast to explore its agreement with observations and the implications for the lifetime of RONO<sub>2</sub> and impacts on atmospheric NO<sub>x</sub> removal and recycling. The paper is very well-thought out, executed, and written. It makes a nice contribution to the literature in this area. I highly recommend publication in ACP. I have only a couple minor science comments and questions for the authors to consider at their discretion. I also list separately some editorial / wording suggestions. Numbering below reflects the page and line numbers.

Science / general comments. =====

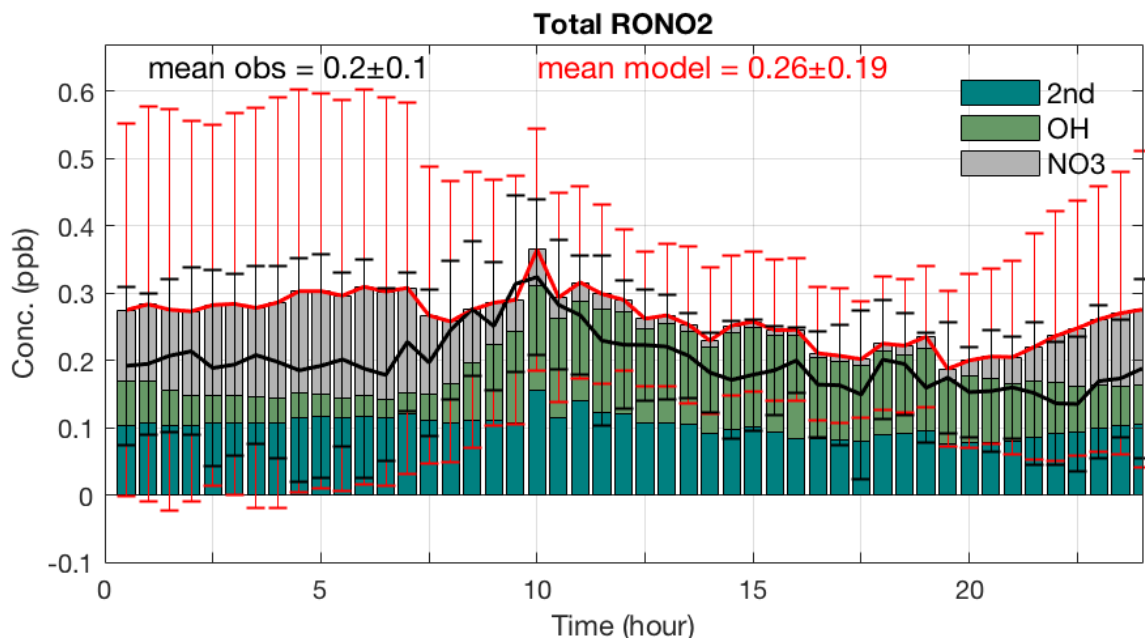
The introduction section is very well written and provides a solid background and well-articulated motivation for the work.

9, 8-20. The discussion here misses the mark a bit. The takeaway one gets from looking at Figure 4 is how flat the entire diurnal cycle is, not just the nighttime data. So “a sharp peak at 320-370 ppt around 10:00” seems inaccurate when the whole dynamic range only spans 200-370 with quite a lot of day-to-day variability (based on the error bars). The daytime decline is obscured by the squished y-axis range of your plot. At the end of the section you give a nice description of the offsetting effects giving rise to the flatness of the data at night, but in fact these offsetting effects give rise to the flat diurnal cycle throughout the 24-h cycle, not just at nighttime. Supplemental Figure S2 shows beautifully how the flat diurnal cycle in fact represents counteracting dynamics of different nitrate species. I suggest merging Figure S2 with Figure 4 to better illustrate this point . . . for example with a separate panel, or perhaps by changing the model trace in Figure 4 to a stacked plot showing contributions from OH, NO<sub>3</sub>, and second-generation nitrates. The observed trace for the total could then be overplotted.

We have merged Figures 4 and S2 and have shown contributions from OH-, NO<sub>3</sub>-initiated and second-generation organic nitrates as stacked bars in the figure. We have also reduced y-axis range to show the diurnal variability more clearly, so that maximum values around 10:00 and slow decline through the rest of the day have become more recognizable. However, we agree with the reviewer, the modeled organic nitrates at nighttime show more uncertain and higher values than observations which make the peak harder to distinguish in simulated diurnal variability. That can be due to mismatch in vertical turbulent mixing in the simulated and actual boundary layers. We have clarified this matter in the text (page 9, line 4).

We have revised the text as follows:

Page 9, 8-9 “Diurnal cycles of measured and simulated RONO<sub>2</sub> have ~~a sharp peak~~ maximum values at 320 and 370 ppt around 10:00, *respectively*, with a slow decline through the rest of the day.”



“Figure 4: Median diurnal cycles of observed (*black*) and simulated (*red*) total organic nitrates at Centreville during the 2013 SOAS campaign. The vertical bars show the interquartile range of the hourly data. The panel includes the mean of the simulated and observed organic nitrates. *Diurnal cycle of the OH-initiated, NO<sub>3</sub>-initiated and second-generation organic nitrate concentrations are shown as the stacked bars.*”

**12, 1-6, this part is a bit confusing and can be better explained. Do you also need to assume a separate lifetime for CH<sub>2</sub>O, or is it assumed to be the same as for RONO<sub>2</sub>? If you apply the analysis to the model slope, do you arrive at the (known) actual model nitrate yield, thus confirming the applicability of the overall approach?**

We have added a reference to Perring et al., that estimated the short lifetime CH<sub>2</sub>O, in the text and described the assumptions more clearly

Page 11, 28-29 “Formaldehyde (CH<sub>2</sub>O) is another co-product to RONO<sub>2</sub> and as Perring et al. (2009b) discussed, the slope of the RONO<sub>2</sub> /CH<sub>2</sub>O correlation is related to the ratio of the production of both species, as both have similar lifetimes (Perring et al., 2009b).”

Using the simulated RONO<sub>2</sub> and CH<sub>2</sub>O we do not exactly derive the isoprene nitrates yield used in the model. The text (page 12) discussing the issue is as follows:

Page 12, 2-6 “The slope would imply an OH-initiated isoprene nitrate yield of 12% (Perring et al., 2009b) if we use a lifetime of 1.7 h at SOAS for RONO<sub>2</sub> as reported by Romer et al. (2016). This is nearly identical to the yield used in the mechanism described in this manuscript. However, the correlation of modeled CH<sub>2</sub>O and modeled total RONO<sub>2</sub> has a smaller slope of 0.085. The discrepancy between the slopes from the simulated and observed data can be attributed to model overestimation of CH<sub>2</sub>O (Fig. S5 in the Supplement).”

13, 18, “Organic nitrates should therefore generally be categorized as short-lived NO<sub>x</sub> reservoirs, which remove NO<sub>x</sub> in a plume, but act as a source of NO<sub>x</sub> in remote regions”. For the purpose of the ensuing section (3.6) you state that you only consider sinks that remove the nitrate functionality, and not sinks that merely represent conversion to a different multifunctional nitrate. But it seems that is not the case for this section (3.5). Is that right? Please clarify. If that’s the case, isn’t the estimated ~3h lifetime an overly-short estimate of the degree to which the RONO<sub>2</sub> are a short-lived NO<sub>x</sub> reservoir?

We derive an ~3hr lifetime of the nitrate functional group to conversion to NO<sub>x</sub> or HNO<sub>3</sub>. Some of the individual first and second generation molecules have longer lifetimes. We have added some detail in the Supplement as follows to be clearer about our thinking:

*“Additional model documentation  
Equations*

*To compute the NO<sub>x</sub> recycling efficiency (NRE) and RONO<sub>2</sub> lifetime ( $\tau_{RONO_2}$ ) we use Eq (1) and Eq (2):*

$$NRE = \frac{P(NO_x)}{Loss(NO_x)} \quad (1)$$

$$\tau_{RONO_2} = \frac{[RONO_2]}{Loss(RONO_2)} \quad (2)$$

*where P (NO<sub>x</sub>) and Loss (NO<sub>x</sub>) refer to the re-released NO<sub>x</sub> due to oxidation and photolysis of RONO<sub>2</sub>, and loss of NO<sub>x</sub> due to the production of RONO<sub>2</sub>, respectively. Loss (RONO<sub>2</sub>) is loss rate of RONO<sub>2</sub>. This lifetime does not include reactions that convert one nitrate into a different nitrate. In contrast, to calculate the lifetime of specific individual molecules we consider all reactions.*

*A simplified scheme, as an example, provides more detail on the approach used.*

<i>Reactants</i>	<i>Products</i>	<i>species to track rates</i>
<i>BVOC + OH</i>	<i>RO2</i>	
<i>RO2 + NO</i>	<i><math>\alpha</math> AN1 + (1- <math>\alpha</math>) NO2</i>	<i>+ <math>\alpha</math> LNOX</i>
<i>AN1 + OH/O3/hv</i>	<i><math>\gamma</math> AN2 + (1- <math>\gamma</math>) NO2</i>	<i>+ (1- <math>\gamma</math>) PNOX1 + LAN1</i>
<i>AN2 + OH/hv</i>	<i>NO2</i>	<i>+ PNOX2 + LAN2</i>

*LAN1, LAN2, LNOX are used to track instantaneous loss of first- and second-generation RONO<sub>2</sub> (AN1 and AN2) and NO<sub>x</sub> at each time step. PNOX1 and PNOX2 track instantaneous re-released NO<sub>x</sub> due to loss of first- and second-generation RONO<sub>2</sub>. Thus, NO<sub>x</sub> recycling efficiency and lifetime of first- and total RONO<sub>2</sub> at each time step are calculated as:*

$$NRE = \frac{((1 - \gamma) PNOX1 + PNOX2)}{(\alpha LNOX)}$$

$$\tau_{AN1} = \frac{[AN1]}{(LAN1)}$$

$$\tau_{RONO2} = \frac{[AN1] + [AN2]}{((1 - \gamma)PNOX1 + LAN2)}$$

”

**Minor technical comments. =====**

**2, 1: ‘At modest concentrations of NOx’ . . . wording is odd as it suggests that it is only at low NOx that RO2 react with NO. Perhaps “Even at modest concentrations . . . “**

We have modified the sentence as follows:

*Page 2, 1-2 “At **high and even** modest concentrations of NO<sub>x</sub>, the peroxy radicals react primarily with NO”*

**3, 27: please also describe the vertical resolution (e.g., number of near-surface levels, etc.).**

This comment is in common with Reviewer 2’s comment. We have expanded the text to include more information about the vertical coordinate.

*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 (~25 m) 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 (~1000 m) that is comparable with the planetary boundary layer depth at midday at Southeastern United States in June 2013.**”*

**9, 1: please clarify if r=0.8 is the correlation for the median diurnal cycle or for the whole timeseries.**

This r<sup>2</sup> shows correlation for the whole time series. We have clarified this as:

*Page 9, 1 “Temporal variability in the total organic nitrates **for the entire time series** is reproduced with little bias (r<sup>2</sup>=0.8 and normalized mean bias (NMB) =32%).”*

**11, 16, “as ozone and total organic nitrates are produced in a common reaction with branches that yield one or the other” . . . It seems this is the case only for the OH initiated nitrates, correct?**

Correct, We have modified the sentence as follows:

Page 11, 16-17 “ *During daytime, ~~as~~ ozone and ~~total~~ organic nitrates are produced in a common reaction with branches that yield one or the other. Therefore, their observed and modeled correlation provides an additional constraint on our understanding of organic nitrates.*”

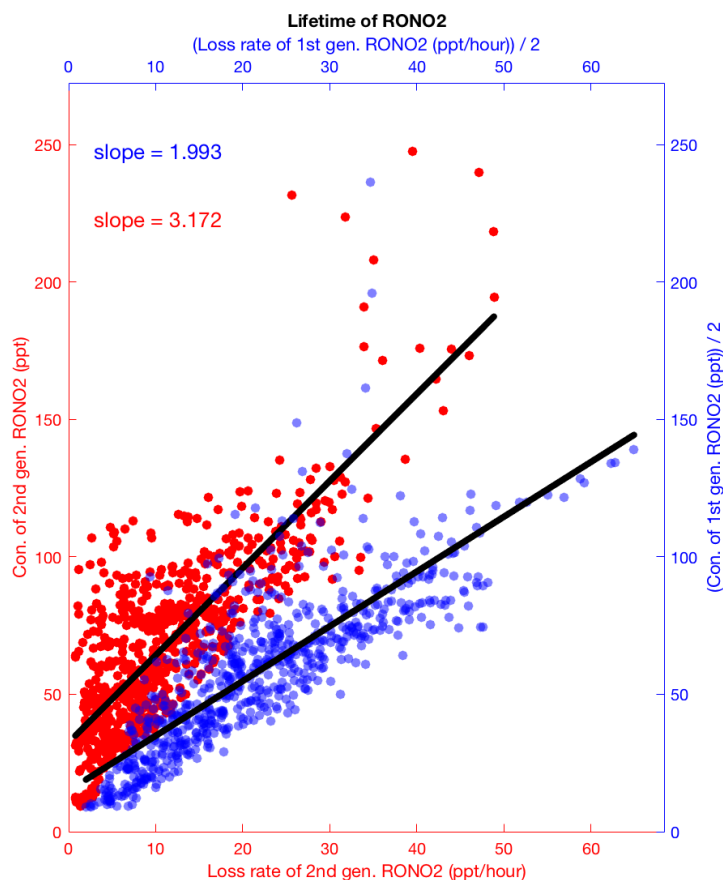
12, 24, “**which causes their concentrations to increase with time in the boundary layer**”, not really increasing with time but rather persisting longer, leading to higher ambient concentrations for a given source, consider rewording

We have changed the text as follows:

Page 12, 23-25 “*This is due to their relatively long lifetime ( $> 100$  h lifetime to oxidation by  $1\text{Å} \sim 10\%$  molecules  $\text{cm}^{-3}$  of OH at 298 K and a similarly long lifetime to deposition (Henry’s law constant of  $\sim 1\text{Matm}^{-1}$ ), Browne et al. (2014) and references therein) that causes ~~their concentrations to increase with time in the boundary layer in comparison to short-lived first-generation biogenic organic nitrates~~ them to persist longer in the atmosphere.*”

**Figure 9, Consider secondary x and y-axis to clarify that the 1st-gen nitrates are scaled by 0.5.**

Done. The figure is revised accordingly.



*“Figure 9: The simulated concentration of 1st- (blue) and 2nd- (red) generation organic nitrates versus their loss rates during daytime at SOAS. Slopes of the linear fit give their lifetimes. The concentrations and loss rates of 1st-generation nitrates are divided by 2.”*

**Wording suggestions. =====**

**2, 11: missing period**

**3, 2: perhaps “from the atmosphere”**

**3, 3: “in simulations of NO<sub>x</sub> and O<sub>3</sub>” or “in simulating NO<sub>x</sub> and O<sub>3</sub>”**

**3, 23-25: awkward, run-on sentence 4, 2: “initial conditions”**

**5, 4: “reacts with OH”**

**5, 13, “yields of”**

**5, 19, awkward, perhaps “to yield either NO<sub>x</sub> or second-generation organic nitrates”**

**8, 24, “at Centreville”**

**9, 2: “observational mean”, “found to be”**

**9, 3, “the highest bias in the model median values and variability”**

**9, 22, suggest “The composition of our model-simulated organic nitrates during . . .”**

**10, 14, suggest “that suggests a larger fraction of these nitrates is subject to . . .”**

**10, 21, “isoprene oxidation by NO<sub>3</sub>”**

**11, 5, “the contribution from”**

**11, 6, “from the observations of the measured”**

**11, 12, “contributes 27% of the total”**

**11, 13, “the rest of the simulated”**

**11, 32, “of background CH<sub>2</sub>O”**

**13, 6, “results in less efficient”**

**13, 31, “and then estimate”**

**14, 16, suggest deleting “from each other”**

**Fig 1 caption, “Re-release”**

**Figure 3 caption, “for the average”**

**Figure 4 caption, “includes the mean”**

**Figure 6, 7, and 9 captions, “during daytime at SOAS” rather than “at daytime during SOAS”**

**Figure 7 caption, “of background”**

**Figure 8 caption, “production” and “averaged over the boundary layer”**

**Figure 9, “Concentrations” should not be capitalized.**

**Figure 11 caption, “recycling efficiency”**

All wording suggestions are applied to the text.