

Interactive comment on “A comprehensive organic nitrate chemistry: insights into the lifetime of atmospheric organic nitrates” by Azimeh Zare et al.

Anonymous Referee #1

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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 RONO₂ and impacts on atmospheric NO_x 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

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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, NO₃, and second-generation nitrates. The observed trace for the total could then be overplotted.

12, 1-6, this part is a bit confusing and can be better explained. Do you also need to assume a separate lifetime for CH₂O, or is it assumed to be the same as for RONO₂? 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?

13, 18, “Organic nitrates should therefore generally be categorized as short-lived NO_x reservoirs, which remove NO_x in a plume, but act as a source of NO_x 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

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lifetime an overly-short estimate of the degree to which the RONO2 are a short-lived NOx reservoir?

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 . . . "

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

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

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?

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

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

Wording suggestions. =====

2, 11: missing period

3, 2: perhaps "from the atmosphere"

3, 3: "in simulations of NOx and O3" or "in simulating NOx and O3"

3, 23-25: awkward, run-on sentence

4, 2: "initial conditions"

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5, 4: "reacts with OH"

5, 13, "yields of"

5, 19, awkward, perhaps "to yield either NOx 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 NO3"

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 CH2O"

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

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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”

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