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Interactive comment on “Organic nitrate aerosol formation via NO_3 + BVOC in the Southeastern US” by B. R. Ayres et al.

Anonymous Referee #2

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General comments:

In this manuscript the authors analyze data taken during the SOAS campaign to estimate the molar yield of particle-phase organic nitrates from nitrate radical (NO_3) oxidation of BVOCs. Briefly, they calculate NO_3 loss due to oxidation of BVOCs using measured concentrations of BVOCs, estimated concentrations of NO_3 and literature values of the BVOC + NO_3 rate constants, and compare that to the total amount of particle-phase organic nitrates measured using two instruments (AMS and TD-LIF). The subject of the manuscript is of general interest to the ACP community. However, important details on the data analysis are missing, some uncertainties are glanced over, and some results may be overstated considering those uncertainties. In summary, I recommend publication after major revisions and consideration of my specific

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comments below.

Specific comments

1. Measurements of particle-phase organic nitrates

The authors use measurements of organic nitrates from an AMS and a TD-LIF instrument but provide close to no information on the data analysis from those instruments. For example, for the AMS:

- How were organic nitrates separated from inorganic nitrates (e.g. what NO/NO₂ ratios were assumed or measured for organic and inorganic nitrates) and what uncertainty is associated with that separation (and the associated molar yield estimate)?
- How was the collection efficiency estimated (which influences the total mass concentration), and what is the uncertainty in that estimate? How do total concentrations from the AMS compare to concentrations of those species measured using other instruments?

The authors further state that particle-phase ON concentrations measured by the TD-LIF instrument were twice as high as concentrations measured by the AMS “for unknown reasons”. This should be discussed further and at least potential explanations should be provided. Is the uncertainty in measurements from these two instruments potentially high enough to explain the differences?

2. Calculation of NO₃ss

The concentrations of NO₃ were calculated assuming steady state since NO₃ concentrations were below the detection limit of the cavity ringdown spectrometer throughout the campaign. Concentrations of NO₃ are essential for the analysis and conclusions presented in the manuscript. Therefore, the uncertainty associated with these estimated NO₃ concentrations should be quantified in the text. Also, what is the detection limit of NO₃ in the cavity ringdown spectrometer? Are the calculated/estimated concentrations always below the detection limit? If not this could indicate a problem in

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either the measurement or the estimation method.

3. Figure S2: the information in this figure (measured and calculated/predicted N₂O₅) is important to evaluate the calculated NO₃ concentrations; however it is difficult to obtain that information from the figure. A scatter plot of measured vs. calculated concentrations with correlation coefficient would seem more appropriate. Also, can the imperfect agreement between measured and modeled N₂O₅ be used to quantify uncertainties in the calculated NO₃s? What NO₃ concentrations would be consistent with the measured N₂O₅ concentrations and how do those NO₃ concentrations compare to the calculated concentrations currently used?

4. Pg. 16244, line 10: does it make sense to compare AMS PM nitrate to total nitrate measured by the TD-LIF when we know that the PM nitrate measurements of these two instruments differ by a factor of 2?

5. Pg. 16246, lines 21-24: These lines seem to imply that a molar yield can be determined from plots such as Fig 6. This seems a bit optimistic considering uncertainties and other processes which may be taking place. It seems more appropriate to state that the slopes are consistent with these molar yields assuming that no other processes are taking place.

6. Pg 16247, lines 5-8: The results of Lee et al., 2015 are important to this study. If the paper is still not available additional information should be provided in the supplement of this study. In this case, the rapid loss of PM nitrates observed by Lee et al. should be discussed further. What are potential reasons for this loss (PM hydrolysis of ONs?) Also, what would be the molar yields of organic nitrates after accounting for this rapid loss? In other words, rather than simply state that the molar yields are a lower bound estimate, could the authors also provide an updated estimate accounting for the effects of that observed loss of PM nitrate?

7. Pg. 16247, lines 26-28: The authors state “Less than 0.5% of total particle-phase organic nitrates observed with the CIMS (Lee et al., 2015) were isoprene oxidation prod-

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ucts, suggesting that most of the isoprene nitrate products remain in the gas phase.” This statement seems to assume that 1) We know the identity of all isoprene nitrate products and 2) The CIMS can accurately measure and quantify all of these products. It is not clear whether these assumptions are justified. More information needs to be provided (again, this information may be in Lee et al., which is not yet available) or the statement needs to be modified.

8. Pg. 16248, line 1: It is not clear to me that these scatter plots can reveal the oxidative source as stated here. It seems more appropriate to state that the scatter plots are consistent with one product being more likely associated with NO₃ oxidation than the other.

9. Figure 1. This figure could be made clearer by increasing font sizes and the size of the marker indicating the location of the field site.

10. Figure 2. It is a bit difficult to see if and when NO₃ss and AN concentrations correlate. Please consider overlaying these traces or otherwise making the figure clearer (e.g. providing a scatter plot). Are the PM nitrate measurements (black trace) from the TD-LIF, AMS or CIMS instrument?

11. Figure 4. What are the uncertainties associated with these NO₃/N₂O₅ losses?

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 16235, 2015.

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