

***We thank the reviewer for their valuable comments. We have addressed each comment below in bold italic text, and indicate where necessary the corresponding changes we have made to the manuscript.***

Anonymous Referee #1

General Comments

In general, this is a very well written manuscript focused on experiments that investigated secondary organic aerosol formation from isoprene oxidation under low humidity scenarios in which nitrogen oxide levels were varied. It includes an assessment of the molecular formulas of the constituents, as well as their volatility. A comparison is made to volatility (vapor pressure) prediction methodologies, as well as to recent field results. It is certainly a topic of much current interest in the atmospheric chemistry community and is appropriate for ACP. Scientifically, there are no major faults with the paper, as it is standard methodologies (chamber at PNNL, for example – please do not misinterpret, as I recognize the difficulty of doing chamber measurements) along side those that are considered cutting edge (FIGAERO, for example) but evaluated and tested.

However, at times, I felt as if I were reading two papers that had been combined into one – that is, there could have been one manuscript that focused on these experiments with a comparison to field results; there are certainly sufficient data to do so. A second manuscript could have focused on the comparison of the volatility measurements to vapor pressure predictive capabilities. While the inability to predict vapor pressures of SOA constituents is not a new finding, the depth to which this area can be probed with the FIGAERO measurements is new and novel – perhaps warranting a second manuscript? This would certainly improve the readability of this manuscript. There were not significant issues with the writing, but the length and density of the manuscript made it slightly difficult to read.

Overall, I have no trouble recommending publication (following the authors addressing relatively minor specific comments below) based on its timeliness, topic, and high quality science. However, I would encourage both the editor and the authors to consider whether the manuscript could be split, simply to improve readability and perhaps to increase impact.

***We appreciate the referee's concern, and we have removed section 3.5 and figure 8 regarding the SOAS field data.***

Specific Comments

It might be helpful to include a short figure that shows the chemical structure of specific molecules that are included in the discussion (ISOPOOH, ISOP(OOH)<sub>2</sub>, IEPOX, etc.) for the individuals who might not think about this on a daily basis.

Responses to Referee #1

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***We added a simple schematic showing isoprene and its major first and second generation oxidation products at both low and high-NO<sub>x</sub>. High NO<sub>x</sub> arrows are highlighted in blue.***

Typo, p. 6, line 144, no need for the word “the”

***Fixed***

Typo, p.7, line 168, “were” should be “was” (suite is singular)

***Fixed***

Typo, p. 8, line 192, programmed has two m’s

***Fixed***

In Figure 1, it might be beneficial to show subsets that allow for seeing shorter periods of time. The length of time included/compressed on the x-axis makes seeing detail nearly impossible.

***We added a supplemental online document with enlarged versions of figure 1 to show more detail. We prefer to show all the data collected in this case given the continuous flow approach used.***

On page 10, lines 227 and 231. What is the basis for the factor of 1.5 to correct for wall losses?

***The correction is determined by comparing the size distributions of ammonium sulfate particles in the inlet and exit flows of the chamber, prior to any SOA deposition. The size dependent particle wall-loss rate is then calculated based on the known chamber residence time and the difference in the number size distributions. The methods to determine the particle wall loss corrections are explained in more detail elsewhere [Liu et al., 2016] for this set of experiments. We refer readers to that paper more clearly now when discussing particle wall loss corrections.***

Typo, p. 16, line 365, data suggest, not suggests

***Fixed***

P. 19, third sentence of paragraph beginning on line 435 could be re-written for clarity.

***Reworded to:***

*However, the disagreement for  $C_5H_{12}O_6$  (Fig. 5, bottom left, circles) cannot be explained solely by thermal decomposition of lower volatility material for two reasons: the thermogram shape is nearly Gaussian and therefore behaves like a single component, and the predicted  $F_p$  is much larger than measured (opposite to the above situation).*

On page 20, with the discussion of use of the measured  $T_{max}$  to predict the  $F_p$  for comparison to measured  $F_p$ : Perhaps I am missing something, but this seems like a circular argument. It should be the case that a measured parameter that is related to  $F_p$  should do a better job predicting  $F_p$  than something unrelated like the vapor pressure estimation technique. I don't think that this adds very much to the paper. I do find the information that allows an investigation of predicted  $F_p$  as a function of molecular formula to be quite interesting and useful though.

***We have tried to improve this section as the reviewer is perhaps missing what we think is an important distinction. The measured  $F_p$  depends upon measured gas and particle phase concentrations of a compound the predicted  $F_p$  depends upon (among other parameters) the  $C^*$  and total OA. In comparing measured and modeled  $F_p$ , there is an initial assumption that gas-particle equilibrium is achieved, and that the  $C^*$  is known. With the FIGAERO, we can independently constrain the  $C^*$  from the thermogram to use in the predicted  $F_p$ . That is, the temperature where a compound's signal reaches a maximum ( $T_{max}$ ), is indicative of its  $C^*$  [Lopez-Hilfiker et al., 2014] but is largely independent of that compound's condensed-phase concentration. Thus using the FIGAERO measurement of  $C^*$  can improve the prediction of  $F_p$  so that issues related to the validity of gas-particle equilibration timescales or the role of thermal decomposition during measurement of particle composition can be the focus of assessing causes of disagreement between theory and measurement (see [Lopez-Hilfiker et al., 2014; Lopez-Hilfiker et al., 2016] ). The following sentences have been added in a short succeeding paragraph to clarify its importance:***

*There are a number of possible reasons why measured and predicted  $F_p$  do not agree, with one being that our methods to estimate  $C^*$  are flawed. This potential source of error can be addressed directly with the FIGAERO-CIMS thermogram, independently of the measured  $F_p$ , thereby allowing for a more robust assessment of whether (i) the assumption of gas-particle equilibrium is reasonable, (ii) there are possible biases in the measured  $F_p$  due to thermal decomposition, or (iii) the  $C^*$  estimation methods are valid. The above analysis demonstrates that all possibilities arise in this data set.*

On page 21, lines 473-475. Please reword for clarity. Which models predicted higher  $C^*$ ? And aren't group-contribution methods models? Perhaps word choice needs to be adjusted (or explain what the difference is).

**Agreed, group-contribution methods are models, although we use “method” here to refer specifically to the group-contribution calculations, while “model” refers to a continuum solvent model [Kurten et al., 2016] and 0-D box model [Valorso et al., 2011] which are more computationally expensive than the group-contribution methods. We have changed the wording throughout the text to be consistent, as well as altering this sentence to include the specific models:**

*Our observations suggest this assumption is incorrect, at least to the extent employed in these methods, and is supported by previous work that found group-contribution methods predicted significantly lower  $C^*$  than two computational models, the conductor-like screening model for real solvents (COSMO-RS) [Kurten et al., 2016] and the generator for explicit chemistry and kinetics of organics in the atmosphere (GECKO-A) [Valorso et al., 2011], did for compounds with multiple functionalities.*

Page 23, line 525. Does the change in viscosity imply a change in chemical composition? Do the measurements reflect that somehow?

***We note that the  $T_{max}$  shift occurs for compounds with the same chemical composition and thus we assume that the compounds have the same structure. It is unclear why this  $T_{max}$  shift occurs, and we can therefore only suggest possible explanations. We do not have direct measurements of the viscosity of the particles.***

On Figure 5, for predicted  $F_p$  (based on equation 1 and an estimated  $C^*$  from group contribution methods), a COA is needed. What value was used here?

***We reworded the sentence starting on line 418 to specify where  $C_{OA}$  came from:***

*$F_p$  were predicted using equation 1 with  $C_{OA}$  measured by the AMS and  $C^*$  calculated via the EVAPORATION group-contribution method [Compernelle et al., 2011], which generally gave similar estimates as the Capouet and Muller approach [2006].*

***Note: there was an error in the pie chart (figure 4) where we were previously not accounting for collection volume for the “other” portion of the pie. The updated figure does not change our conclusions.***

## References

- Capouet, M., and J. F. Muller (2006), A group contribution method for estimating the vapour pressures of alpha-pinene oxidation products, *Atmospheric Chemistry and Physics*, 6, 1455-1467.**
- Compernelle, S., K. Ceulemans, and J. F. Muller (2011), EVAPORATION: a new vapour pressure estimation method for organic molecules including non-additivity and intramolecular interactions, *Atmospheric Chemistry and Physics*, 11(18), 9431-9450, doi: 10.5194/acp-11-9431-2011.**
- Kurten, T., K. Tiusanen, P. Roldin, M. Rissanen, J. N. Luy, M. Boy, M. Ehn, and N. Donahue (2016), alpha-Pinene Autoxidation Products May Not Have Extremely Low Saturation Vapor Pressures Despite High O:C Ratios, *J. Phys. Chem. A*, 120(16), 2569-2582, doi: 10.1021/acs.jpca.6b02196.**
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- Valorso, R., B. Aumont, M. Camredon, T. Raventos-Duran, C. Mouchel-Vallon, N. L. Ng, J. H. Seinfeld, J. Lee-Taylor, and S. Madronich (2011), Explicit modelling of SOA formation from alpha-pinene photooxidation: sensitivity to vapour pressure estimation, *Atmospheric Chemistry and Physics*, 11(14), 6895-6910, doi: 10.5194/acp-11-6895-2011.**