

Atmos. Chem. Phys. Discuss., referee comment RC2
<https://doi.org/10.5194/acp-2021-251-RC2>, 2021
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Comment on acp-2021-251

Anonymous Referee #2

Referee comment on "Modelling the gas–particle partitioning and water uptake of isoprene-derived secondary organic aerosol at high and low relative humidity" by Dalrin Ampritta Amaladhasan et al., Atmos. Chem. Phys. Discuss.,
<https://doi.org/10.5194/acp-2021-251-RC2>, 2021

Review of Amaladhasan et al "Modelling the gas–particle partitioning and water uptake of

isoprene-derived secondary organic aerosol at high and low relative

humidity".

General Comments: In this manuscript, the authors couple a gas-phase mechanism to an equilibrium partitioning model to simulate SOA formation from isoprene ozonolysis in the CLOUD chamber. The main focus of the paper is in understanding the role RH and inorganic seed particles play in determining SOA yield. The model is also used to predict whether liquid/liquid phase separation occurs and under what RH conditions. The topic is of interest to the readers of ACP and fits in well with the journal. The modeling techniques are state of the art. The figures are relatively clear and appropriate. With that said, I had a very hard time evaluating this manuscript for reasons given hereafter and therefore recommend it be revised significantly and potentially re-reviewed before publication.

First, the manuscript is somewhat long, dense, and tends to wind between several different experimental conditions. I suggest editing for length and clarity; the authors can probably cut 1/3 of the length of the paper without losing much. Many sections read like a

thesis with descriptions of the model results, but lack context regarding what the results mean or the real-world implications of the results. Second, the references to the experimental description and data are to a thesis, which is almost 200 pages long. This reviewer didn't read through the 200 page thesis to try to figure out what was done. The experimental results are key to evaluating the modeling. The authors should include a short section describing some aspects of the experiments that a key to understanding the results. Many of these uncertainties are listed below in the specific comments section. There are a lot of small mistakes, contradictions, confusing sections, etc. Any one of these is small on its own, but they add up to make it difficult to understand how robust the results are and frustrating to try to follow the manuscript.

Most importantly, the authors are trying to probe very small difference in the SOA yields between chamber experiments conducted at different RHs and with different seed. In most cases, the difference in absolute yield is between experiments is around 1%. The authors need to convince the reviewers that this 1% difference is significant. The model is tuned to match results at one particular set of conditions (e.g. 35% RH) and then applied to the other condition. It appears that only one experiment at each condition was conducted. Experiment to experiment variability for chamber experiments is going to be larger than 1% yield. The authors indicate that a simple gas-phase wall loss correction was applied and the same correction appears to be used across the different conditions. In addition, the uncertainty on the measurements themselves is 50%; I don't believe this includes any experiment reproducibility error. These errors will all add up. Finally, the gas-phase mechanism needed to be adjusted between the seeded and unseeded runs. There is little reason to believe that the actual gas-phase chemistry produces a factor of almost 2 difference in the produce yield. So obviously the model is not capturing all the processes that determine yield. In sum, I find it hard to imagine that a 1% difference in yield in a large SOA chamber experiment is significant. The authors haven't show repeated measurements to establish this level of accuracy and reproducibility was achieved. This makes it very difficult to evaluate whether the model results are robust or whether they are essentially modeling experimental noise.

Specific Comments:

Through paper: The authors refer to Fuchs 2017 for a description of experimental conditions. This reference is to a thesis, which struck me as somewhat unusual. Was this work never published in a journal? Given that the measurements are central to the modeling, it would be good to expand somewhat more on the conditions.

Through paper: What fraction of isoprene reacts with ozone vs OH? Significant OH will be produced given the high concentration and continuous input of isoprene and ozone.

P2/3 Lines 33-2 : Sentence needs revision, it is unclear.

Page 3: Introduction is somewhat difficult to follow because the authors skip and intermingle between ozonolysis and photochemical oxidation. For example, the second paragraph of page 3 is discussing ozonolysis of MVK and MACR, which predominantly form from OH initiated oxidation.

Page 4, lines 8 – 11. This statement is somewhat misleading. Regarding the contribution of isoprene ozonolysis SOA, Kleindienst et al 2007 conclude: *"Thus, even in light of the increased yield for the ozonolysis of isoprene measured in this study, the ozonolysis reaction probably remains a minor contributor to secondary organic aerosol in PM2.5 from the atmospheric oxidation of isoprene."*

Page 5, Section 2.1

This section is confusing in a few respects. First, the authors mention that NO_x ratio was varied, but later say experiments were conducted under low-NO_x conditions. Second, they discuss operating in the chamber with cloud processing, but it isn't clear how this was taken into account by the model. If cloud droplets were formed wouldn't aerosol either be rained out or undergo a completely different type of processing?

Page 5, Section 2.1 – Were the aerosol particles dried before SMPS and AMS measurements? Are there any measurements of the liquid water content of the particles under the experimental conditions?

P5 Lines 30 – Were the isoprene measurements used in any way in the model? Why not just input the measured concentrations? Did the modeled isoprene and reacted isoprene

agree with the measurements?

P6 Lines 6 – 8. Was the aerosol density assumed to be 1.3 or calculated according the parameterization?

P6 Lines 9 – 10. Earlier you said the chamber was run in continuous-flow mode. Here yields are calculated as a function of time. Are you using transient concentrations while running in continuous-flow mode or batch mode? The table indicates a single set of conditions. It is confusing where the yield is coming from?

P9 Lines 2-5. I don't understand what you are trying to say here.

2.3.2. It is a little hard to understand why the MCM was used or what it was used for. In the end, you tune the model to produce all the generic compounds that partition into the condensed phase? Why go to all the trouble of using the MCM? Why not just react isoprene at the know rate constant to make a few products and then tune that output? Most of the representative products are from OH oxidation, but the experiment was primarily an ozonolysis experiment.

Page 12 – 13 – This entire section is extremely confusing. Presumably, the authors are using the MCM to calculate reacted isoprene and the amount of first-generation oxidation products. Therefore, it isn't clear why these two pages of text are so complicated and confusing. Analytical solution for time-dependent concentration of a particular species in continuous-flow mode are widely available in the literature and not difficult to solve. Why is there a need to introduce a tracer reacted isoprene concentration when the MCM should already calculate this?

P 13, line 13 - Why average over 30 minutes if the chamber is at steady state and you are using model outputs? Shouldn't the average over the 30 minutes be the same as at any time during that interval if the chamber is at steady state? Was the chamber at steady state?

P 13 line 17 - 19. Not clear what you are trying to say here.

P13, lines 21 - 22. Conditions weren't stable if the water saturation is changing, particularly given you're investigating the role of RH on yield.

P13 - If there was cloud formation during the experiments, wouldn't this impact yield? Wouldn't any cloud-processing reactions alter the SOA composition? How were these taken into account?

P15, lines 24 - 28. How unique are the solutions you arrived at for these scaling parameters? With 6 free parameters, I imagine there is a large solution space and many different solutions may describe the yield equally well or nearly equally well given the measurement uncertainty.

P16 lines 23-24 and throughout document. Since yield is dependent on SOA mass loading, when listing yield, mass loadings also need to be specified. Similarly, when comparing yield under different RH and T, list the mass loading.

P17, lines 11-14. Table S1 actually shows the pseudo-molecular yields for the surrogate compounds. I could not find the measured and modeled SOA mass concentration vs reacted isoprene in the document. This is crucial to understanding what was done, so it really needs to be made available. There are only a few entries in Table 2 in the main text that do not appear to correspond to the data in the figures.

P17, lines 20-30. The data shown in Figure 3 seem to indicate a bimodal distribution of yield values, with some of the values aligning well with the model data and other measured values much higher than the modeled data. Were these all a single experiment? There is only one experiments for each set of conditions listed in Table 2, so it isn't clear where the multiple datapoints come from. Are they from different points in the equilibrium or different points as the system approached equilibrium or something else? Were the experiments repeated more than once for a given set of conditions? From Table 2, it appears only one experiment was run for each condition.

It isn't necessarily surprising that all the data don't fit a single curve perfectly due to variability in experiments. But what does this mean for your modeling? The "outlier data" have approximately 1.5x the yield of the other data. This is similar or even greater than the differences between the 35 and 85% RH experiments. Given that the model was tuned to the lower yield data for the 35% yield case, how do you know the differences in the model are significant? If you tuned the model to the outlier data in the 35% case how will it fit the 85% RH data?

P 19, First paragraph – Yield needs to be compared at similar SOA mass loading, since it is dependent on mass loading at these concentrations. How does yield change at a similar mass loading? Also the absolute difference in yield is only 1%. In general, experiment-to-experiment variability is going to be larger than 1% in absolute yield. How many experiments are evaluated here; is there only one per condition? Given all the uncertainties with wall loss, experimental variability, etc. is a 1% difference in yield significant? Is there reason to believe wall loss isn't changing with RH? Would changing the gas-phase wall loss as a function of RH account for the differences in observe yield?

P19, lines 16 – 21. How does the computed particle-phase water content of the SOA compare to measurements of the hygroscopic growth factor? The mass fraction of water at 80% RH appears to be about 25%. This seems much larger than the hygroscopic growth factor typically measured for pure SOA at 80% RH.

P21, lines 23 – 25. What were the conclusions of this study? Can they be used to support your hypothesis that differences in the vapor wall loss are responsible for the differences in yield? It seems out of place to just say studies have been done.

P21 Lines 26-27 – I'm not sure what is meant here. You didn't measure the temperature dependence of the vapor pressure of individual compounds.

P21 lines 29 – 30. What fraction of isoprene reacted with OH vs ozone in the experiments? This should be reported in the manuscript.

P21 -22, lines 31 – 24. The discussion here shifts to isoprene photooxidation SOA. This is somewhat confusing. I'm not sure it is particularly relevant to this paper unless a significant fraction of isoprene reacted with OH.

P21 lines 19 – 20. Wouldn't a similar logic apply to the RH dependence as well? In the unseeded experiments the model is tuned to the 35% RH results.

P24 lines 1-2. OH is formed from ozonolysis of isoprene with significant yield.

P24 lines 3-6. It isn't clear what you mean when you say the chamber was run under different conditions. The only significant difference I see is the T and the seed identity. Why would a 5 C difference in temperature perturb the gas-phase chemistry such that a different product distribution was necessary? Doesn't the fact that a single gas-phase chemistry product distribution fails to describe these experiments with different seed but similar gas-phase chemistry is similar indicate that something more is going on?

P24 Lines 10 – 14. If the vapor wall loss is indirectly impacted by the RH via the condensational sink rate, wouldn't this also impact your results in the seed-free case? Why does it matter in the seed case, but not the seed-free case?

P25, line 13-14. Here the authors indicate the AMS was used to measure SOA mass. On page 6 the authors indicate the SMPS was used to calculate SOA mass. Please clarify what measurement was used under which conditions. If the SMPS was used in unseeded cases and the AMS in the seeded cases, was a comparison done of the AMS and SMPS derived masses? Are they similar?

P30 Lines 16 – 32. This is confusing. Are you saying you used the downscaled molar yield derived from the seeded experiments to conduct a seed-free model run? If so, I'm not sure what is learned, since the product yields derived from experiments in the seed-free cases were significantly larger than what was used in the comparison. What exactly is learned by comparing a model where the molar yields don't represent what was actually observed in the seed-free case?

P31 line 11. What is meant by an SOA yield "by volume"?