

Interactive comment on “ α -Pinene secondary organic aerosol yields increase at higher relative humidity and low NO_x conditions” by Lisa Stirnweis et al.

Anonymous Referee #2

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This manuscript presents experimental and modeling efforts in order to describe the formation of secondary organic aerosol (SOA) from photo-oxidation of alpha-pinene under various humidities and NO_x concentrations. Also the role of seed aerosol composition is studied in relation to liquid water content of particles. The experiments clearly show that varying the above parameters cause large, and complex, changes in the SOA yields. The authors then attempt to draw further conclusions by phase partitioning calculations. While I find the model results to be less convincing, the model is described in detail, and thus readers can assess the validity of the different assumptions adequately. The paper fits the scope of ACP, and should be considered for publication following the below comments.

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General comments:

While the language of the manuscript is very good, I found several descriptions and conclusions hard to follow. Especially the causality in certain sentences should be clarified. As an example, in the abstract it is stated “At low NO_x conditions, equilibrium partitioning between the gas and liquid phases can explain most of the increase in SOA yields at high RH. This is indicated by the model results, when in addition to the α -pinene photooxidation products described in the literature, more fragmented and oxidized organic compounds are added to the model mixtures”. Is the point here that if adding oxidized fragments to the mixture (but not otherwise), the model can explain the increased yields at low NO_x by equilibrium partitioning? The formulation of “indicated . . . when” is presumably the main reason for my confusion. Another example is page 15, lines 24-27: “Accordingly, additional insights into the prevalent mechanisms by which the compounds form and evolve can be gained. For example, highly oxygenated compounds cannot be very volatile without significant fragmentation, whereas oligomerization leads to a significant decrease in the compounds’ vapor pressure without necessarily increasing their O:C ratios.” It is unclear to me how the latter sentence is an insight gained from this work? And the content is in any case quite common knowledge, to some extent even used as an assumption in this work. There are several paragraphs with similar issues in the paper, and I recommend the authors (or preferably even someone external) read through the paper with the aim to check how claims of causality are presented.

Title: Currently, the title only reflects the experimental findings, while more focus is put on the model results in the text itself as well as the abstract. Also, the claim is left too general: is this true regardless of the oxidant (OH, ozone, nitrate radical) or [NO] (only NO_x is mentioned). I suggest revising the title to better describe the content of the paper.

Specific comments:

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P1, line 20: For terminology: SOA yields are not affected by particle wall loss. The measured SOA mass is, and if not accounting for that, one will get an *apparent* yield that is too low. On the other hand, vapor losses will affect the SOA yields in much more complicated ways. While I do not expect the authors to include vapor wall losses into the model at this stage, and it would be extremely hard to do correctly, the authors should acknowledge that there is a wealth of evidence from the last years that neglecting vapor wall loss will influence SOA yields, including e.g. Kokkola et al., 2014 (the first in a line of recent publications on the role of walls in Teflon chambers), Ehn et al., 2014 (detection of “ELVOC” that irreversibly are lost to walls) and Krechmer et al., 2016 (direct measurements of vapor wall losses in a Teflon chamber). The authors should at least note some of these papers and their findings in the manuscript, rather than only citing the papers that support their approach.

P1, line 20: “as a function of absorptive masses combining organics and the bound liquid water content.” This is a confusing formulation. Rather say “. . .absortive mass, defined as the sum of organics and the . . .”.

P2, 18: Why limit this statement to semi-volatile species?

P5, 5-7: What does it mean when stating “similar NO_x/VOC” when no a-pinene is added??

P7, 32-33: What were the ozone concentrations? I would like to see a (supplementary) figure with an example experiment showing at least a-pinene, ozone, butanol and OH concentrations together with the SOA mass.

Fig. 5: Why are figures 5 and 6 discussed before figures 3 and 4?

P12, 9: Please use another word than “corresponding” for these comparisons. It is misleading.

P13, 1-10: This is also consistent with more a-pinene producing more SOA and thereby condensation sink (CS), which in turn can more efficiently compete with the walls as a

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sink of low-volatile vapors. See e.g. the papers cited above. The authors can easily do a sensitivity check for this effect. If there is a large change in particle vs wall loss rates, point 1 should be reconsidered. On the other hand, if the initial seed provides a relatively constant CS (compared to wall losses) for every experiment, then the claim in point 2 that seed concentrations in general are not important seems unjustified, since this was not probed at all in these experiments.

P13, 2: Please clearly distinguish between percentages and percentage points. I expect this should be the latter.

Fig. 4: There is a clear bimodal distribution for most cases, which is also noted in the manuscript. However, I find the explanations and discussion about it lacking. The authors state that particle number increased, but no new particle formation was observed. This needs some further discussion. Where do the particles come from then? Additionally, the bimodality is used as proof for LLPS, which the model also predicts, but I do not find a clear description of why the organics form this bimodal distribution.

Fig. 7&8: Make the contrast between the currently light and full colors more visible. At least on my screen some pairs were hard to distinguish.

P15, 36-37 and related O:C discussion: A variation of 0.03 from 0.45 to 0.48 is considered “almost constant” while an increase of 0.08 is considered significant? And only several pages later in section 4.6 is it noted that the uncertainty in O:C is 20-30%. It is also noted that the O:C values are likely biased low since the latest parametrization for O:C calculations are not used. These things should be mentioned earlier, so a reader can properly assess the meaningfulness of the comparisons done in sections 4.2-4.3. Considering all the above, the tuning of the model to match these values does not in my mind give much more insight into the formation mechanisms of SOA in this system.

P18, 3-5: Is this shown somewhere, or just stated? There were also other places where the formulations are such that I expect there to be a figure showing the result. The authors should consider adding “not shown” in places where the information is not

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visible in any plot or table.

P18, 22-26. There are too many numbers listed in the text, and this is especially true here. Please consider rewriting this.

P18, 19-22 and Fig. 9: It is hard to follow discussion about increase of factors 2-5 from a plot ranging 14 orders of magnitude. Could Fig. 9 be moved to the SI, and some more specific plot included in the main text?

P18, 39-40: I do not understand at all what this sentence is supposed to say.

P19, 7: "sufficient" for what?

P20, 22: Expected based on what?

P21, 28-29: This is too strong a statement in my opinion. Rather say that only with inclusion of the fragments could your model describe both SOA mass and O:C.

P21, 40-P22, 2: Such a statement should be included much earlier in the discussions on bimodality, and not saved to the last lines of the manuscript.

P22, 2: Again, what is this expectation based on? Work in this paper or other work?

References

Ehn, M., et al. (2014). *Nature*, 506(7489), 476-479.

Kokkola, H., et al. (2014). *Atmospheric Chemistry and Physics*, 14(3), 1689-1700.

Krechmer, J. E., et al. (2016). *Environmental Science & Technology*, 50(11), 5757-5765.

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