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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Temperature and VOC concentration as controlling factors for chemical composition of alpha-pinene derived secondary organic aerosol" *by* Louise N. Jensen et al.

Anonymous Referee #2

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Summary:

The authors present a very interesting dataset of secondary organic aerosol (SOA) composition measurements with a High-resolution Time of flight AMS (short: AMS) and offline filters. They investigated the evolution of a-pinene SOA generated via dark ozonolysis in a temperature-controlled chamber either at constant temperatures (20 °C, 0 °C, and -15 °C) or with controlled temperature ramps. They compared the end point composition with offline filter measurements and apply Positive Matrix Factorisation (PMF) analysis to the AMS data. They find PMF factors describing the difference observed in composition due to the changing temperature and factors that capture

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the impact of different precursor concentrations. They conclude from the temperature ramp experiments that the temperature at which the particle formation is more important for the overall particle composition than the final temperature. I think this is a great data set with the potential to give important insights into how temperature and precursor concentration control the chemical composition of a-pinene SOA particles which is important to understand when comparing chamber experiments to ambient measurements. Unfortunately, the presented analysis and interpretation of this data set are somewhat superficial. The authors mostly just describe the data but leave the reader wondering about the implications. I therefore request major revisions of the data interpretation and discussion part in addition to addressing my comments below before this paper can be published in ACP.

Major Comments:

1) One reason the discussion of the results is so unsatisfactory is that the authors do not use the additional information available for these experiments. As one example, take the only small changes in O:C observed in the temperature ramp experiments 2.1 - 2.3. How much did the SOA mass concentration / particle size change in that time? I.e., how much was the existing SOA composition perturbed by the T ramp? With that in mind, how much change can be expected in a value like O:C? I.e., if cooling from 20 °C to -15 °C leads to the condensation of x% of compounds with lower O:C how much does that change the O:C of the original particles? Is O:C sensitive enough to monitor such changes? This is just one example of how the authors can improve the interpretation and explanation of their results. I request that the authors utilise the other available information (part of it is already published in Kristensen et al. (2020) and Quelever et al. (2019)) to support their findings and strengthen the discussion.

2) A second reason is that the authors do not use the results of their presented data set to the full extent possible. They conducted PMF analysis and concluded that the grouping of the factors is connected to the SOA formation temperature. Why do they not use this to investigate composition changes in the ramp experiments (Exp 1.5&1.6,

2.1-2.3)? The PMF chapter (3.1) is mostly describing the marker ions in the different factors and comparing the factors with each other (and one ambient example). But there is no analysis of the temporal evolution of the contribution of the factors during the experiments. Chapter 3.2 is instead focusing on the changes in O:C and the two tracer ions m/z 43 and m/z 44. Kristensen et al. (2017) already covers the temperature dependence of the acid and ester dimer formation in detail. The fact that the AMS f44 values agrees with the LC-MS results is nice. I request a more thorough interpretation of the changes in PMF factor contributions during the experiments which will hopefully reveal the "bigger" picture of the composition changes with temperature and precursor concentration as the PMF analysis utilises all ions detected in the AMS and not just m/z 43 and m/z 44.

3) The paper presents many (factor) mass spectra and compares them stating that they are similar (or not). But the authors do not explain what metric they use to determine similarity (statistical method, ratios of marker ions, "by eye"). If they have not used a objective (mathematical) metric, I recommend using the spectral contrast angle, theta, which is derived from the dot product of two mass spectra, A and B (Wan et al., 2002). A and B are considered similar if theta is between 0° and 15°, somewhat similar but with important differences if theta is between 15° and 30°, and different with theta values >30° (Bougiatioti et al., 2014). This parameter (sometimes as cos theta with values between 0 and 1) has been used for AMS data before (e.g. Bruns et al., 2015; Kostenidou et al., 2009). Such a pairwise comparisons will also help with claims like that the composition of the 0 °C and -15 °C experiments are closer to each other than to the 20 °C case. I request that the authors specify how they determined similarity of mass spectra and provide values/graphs that show the degrees of similarity (can be in SI material).

4) The explanation and labelling of the PMF factors as high/low concentration or temperature is a bit misleading and easily misunderstood. Their labelling/description makes it sound as if the effect of higher precursor concentration is covered by switching

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from Factor 3 to Factor 2. But the higher cOA (organic aerosol particle mass) also impacts the contribution of the other factors. As an example, Factor 4 (low T) increases its contribution at all temperatures when the VOC concentration is increased. In a similar way, the contribution of Factor 2 (high concentration) strongly depends on temperature (e.g. increasing for 10ppb cases with decreasing temperature). They authors do explain the connection of partitioning with C* and cOA in the introduction in general, but they do not clearly state how the factors fit into this framework. The authors need to clarify how and why the factors are related to cOA and temperature, i.e., interpret the factors with regard of volatility.

5) Continuing the point from the previous comment, from the limited explanations provided in the text, I derive that the authors made the assumption that the factorisation in PMF depends on the condensation behaviour of the compounds which is governed by the temperature and the increasing cOA. I.e., the increase in contribution of factor 4 with time in Exp 3.2 and 3.3 would thus be explained by higher volatility material condensing as cOA increases. But why would then Factor 2 decrease already before the peak in mass concentration is reached? Could that not be connected to ongoing chemical processes? In this paper, there is no information about the consumption of the precursor and thus on how long reactions may be ongoing. How do the different reaction rates at low/high temperature and/or different precursor concentrations affect the oxidation products? This is especially interesting for the T ramp experiments (1.5 & 1.6). The authors have to at least mention if or how ongoing chemistry would impact the PMF factors and volatility of reaction products. If the authors merely want to compare the final composition of the formed particles, they need to clarify that and provide information how they determine the “end point”.

6) As in many papers with AMS data, the authors use the O:C values as a parameter for the oxidation level of the investigated SOA particles. However, if the H:C values also change (as they point out when discussing the van Krevelen diagram in Fig 4b), the case is not that simple and the average oxidation state of carbon (OSC, Kroll et

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al. (2011)) may be the better parameter representing the degree of oxidation in the particles. As an example, for Exp 3.3 (50 ppb, -15 C) in Fig 4b, I read a change for O:C & H:C values from 0.28 & 1.62 to 0.33 & 1.705, respectively. Calculating OSC as OSC = 2*O:C – H:C gives 1.05 and -1.06 for the start and end of the experiment, i.e., the average oxidation state of carbon did not change. As another example, the OSC values of factors 2 and 4 are almost identical although the O:C values differ. Do the authors have a reason why O:C would be a better measure of the level of oxidation in their experiments than OSC? If not, they should change to using OSC to account for changes both in O:C and H:C and adjust their interpretation accordingly.

7) The current data interpretation relies heavily on the differences and changes in O:C (and H:C) values and the behaviour of f44 and f43. But there is no discussion of uncertainties/measurement errors for these values. Also, the authors do not state if they calculated the values for all data points, or did they apply a minimum mass concentration. Typically, O:C values become very noisy at AMS mass concentration < 0.5 ug m-3. I.e., the values at the start of each experiment may be less reliable. The authors need to add a comprehensive discussion about the uncertainties of O:C and H:C.

8) The authors completely ignore the changes in RH during their experiments. This may be fine for the constant temperature experiments as all are at RH < 15% (i.e., dry conditions). But for the ramp experiments this has to be considered as RH values as high as 80% (end of Exp 2.1) will lead to considerable amounts of water in the particles. The ramp experiments 2.1 - 2.3 are technically evaporation/condensation experiments assuming that most chemical processes have ceased that late in the experiment. Uptake and evaporation of vapours is strongly connected to the phase state of the particle (solid vs. liquid like) and will change with temperature and RH (Li et al., 2019; Zhao et al., 2019). Analysing the change in contribution of the factors should yield more insights into the effect of temperature and RH. The authors need to at least mention the possible impact of changes in RH during/between experiments.

9) It is good that the authors present results from other than the chosen PMF solution. But they do not provide enough information why the 4-factor solution was selected. Providing Scaled Residual values for all ions is a good start for such a discussion. However, I am not capable of deriving anything from the presented graphs (Fig S2-S4) other than that there are many red boxes and lines. As this is HR data, most boxes overlap making it very difficult to see any differences between the three figures. I recommend looking instead at the Relative and Scaled residual as time series. This will also show more directly for which experiment the additional factors improve the reconstruction. There needs to be more discussion (in the SI material) about why the 4-factor solution was chosen, and the presentation of the supporting graphics needs to be improved to be more accessible for the reader.

10) The Authors compare their data to ambient data by Lee et al. (2016) and conclude that their mass spectra are highly similar to those presented in that paper. This claim is difficult to judge as they are not providing the metric that they used for such comparisons. However, I agree that "by eye" the main patterns for Factor 1 and BSOA1 are similar even though the marker ion m/z 91 = C7H7+ is missing from Factor 1. But Factor 3 exhibits distinct differences (44 higher than 43, higher 55, 27 and 29). And how is 0.39 & 1.59 (O:C and H:C of factor 3) "highly similar" to 0.56 & 1.56 (O:C and H:C of BSOA1)? These values correspond to OSC of -0.80 (factor 3) vs -0.44 (BSOA1). Comparing the van Krevelen diagrams shows that all measurement points in this study (Fig 4b) are outside of the range of measurements in Lee et al. (grey and orange dots in Fig 3). Only Factor 1 (the most oxidised here) is near the edge of the distribution and has similar O:H and H:C values as BSOA1 (the least oxidised in Lee et al, 2019). The authors have to find a better suited example to compare to their results.

11) The authors should compare their results with the findings of Zhao et al. (2019)

Specific comments:

1) What was the time resolution of the AMS?

2) Why was 35 min chosen to start the T ramp in Exp 1.4 and 1.5? How much of the precursor was still left at that time?

3) How large are the uncertainties of estimating density from O:C&H:C? (see also Major comment 7). Is this uncertainty smaller than what would be expected from using average RIE&CE values? Did you collect particle time of flight (pToF) data? Could you not compare the vacuum aerodynamic diameter with SMPS data? Without an uncertainty estimate such small changes as described in Fig S9 cannot be interpreted.

4) OSC can be calculated based on O:C and H:C. Are the trends in OSC during an experiment different from those in the density you calculate?

5) Your Q/Qexp values seem to level of at a value a lot larger than 1 which may be caused by using a too small measurement error value. Have you checked your measurement error estimate? Could there be additional sources of uncertainty?

6) In addition to Q/Qexp values the ratio of explained variance to total variance may be worth looking at when discussing which PMF solution was selected.

7) The mass spectra presented in e.g. Fig 1b or Fig 3 look like the HR data was recombined to UMR resolution and colour coded by family. If this is the case, this needs to be clearly stated.

8) Did you really use m/z 43 and m/z 44 derived from UMR analysis (using UMR frag tables) for the tracer ion analysis (page 8)? Or did you run the HR analysis and recombine to UMR signals? This needs to be stated.

9) For the second set of ramp experiments (Exp 1.5 and 1.6), it is of interest how much of the gas phase chemistry had already happened when you started the ramps as there should be some temperature dependence for the kinetics. Was all a-pinene consumed? Also, what were the starting gas phase compositions? Was the same amount/type of HOMs formed?

10) As the numbering of Factors in the PMF solutions does not have a meaning (to

my knowledge), you should consider a meaningful numbering, e.g. by the (assumed) volatility of the factors or the degree of oxidation (OSc). This will make the factor description and comparison easier to understand for the reader.

11) It is difficult to see how the relative contribution of the factors change with time in Fig 2. Add the "unstacked" factor time series to the SI material. This will help especially with interpreting the T ramp experiments.

12) What happened in Exp 3.3 around 50 min? There is a bump/shoulder in the time series.

13) When you are interpreting the simultaneous O:C and H:C change for the 50ppb experiments (page 7 last paragraph) you should take into account that in this specific case there is very little change in OSC, i.e., that the average degree of oxidation does not change. This may point towards non-oxidative reactions being the main source for the composition change. Or it might mean that at the same time more oxidised compounds (higher O:C than already in particles) are condensing as they are formed by ongoing oxidation reactions in the gas phase and also more volatile compounds (higher H:C than already in the particles) partition due to the increasing cOA. The net change could then be as you observe.

14) If you argue that compounds condensing at low temperatures are not well captured by the elemental analysis parameterisation, that would also be relevant for ambient measurements. 0 °C is not that uncommon during wintertime or nights, and the SOA mass loadings in your high concentration experiments are not that far off from ambient loadings in more polluted regions. Is it not more likely that you are simply observing condensation of more volatile and less oxidized species in these experiments? The 50 ppb and -15 °C case should have the least volatile compounds condensing as cOA was highest and C* values will be lowest. At higher temperatures, the effect vanishes as that compound class no longer partitions into the particle phase. You may just be probing a different range compounds at the lowest temperature (i.e., compounds that

are too volatile to condense at 20 °C).

15) Why were the T ramps during SOA formation done at 10 ppb and the T ramps at the end of the experiments at 50 ppb?

16) The slope of the O:C values for Exp 2.2 and 2.3 seems to change when T crosses 0 °C. For Exp 2.1 it is hard to say. Could there be an effect of “frozen” particles?

17) Figs 4b and 6b reveal some differences between “same” experiments which are not addressed in the text. Exp 2.1 and 3.1 show a bigger difference between each other than Exp 2.1 and 1.1 (Fig 5). In Fig 6, Exp 2.1 data is not visible. However, Exp 2.2 has decreasing f44 and f43, but Exp 3.2 is constant. f44 decreases in Exp 3.3 as much as it increases in Exp 2.2. I would not call that “good reproducibility” (page 8).

18) In Fig 6b, the arrow indicates a decrease of f43 for Exp 3.2 but the text states an increase for all experiments at -15 °C. Or is the arrow the wrong way round?

19) How much of the SOA mass is explained by the acids and esters detected in LC-MS? It is not simply (18+4)% and (38+11)%

Language and presentation:

+ Decide if you want to separate adverbial terms at the start of a sentence by a comma. In many cases, you used a comma. In other cases, you did not.

+ Reference entries to Quelever and Rosati are missing.

+ page 2 line 8 “and has it been” -> “and it has been”

+ page 2 line 10 OH and NO3 are not negative ions but radical. Use “·” (dot) not “-“

+ page 2 line 17f put the e.g part into commas or remove comma before “because”

+ page 4 line 35 “The number of factors are chosen. . .” -> is chosen

+ page 5 line 21&23, page 6 line 14 you use the term “CHO” in contrast to CHOgt1. But later you use “CHO1” several times. -> Choose one label.

+ page 6 lines 21-28 this should be together with the previous paragraph as it is still describing the factor MS. Do not just start a new paragraph become the current one is feeling too long.

+ page7 line 36/37 “hydration reactions with carbonyls” -> hydration reactions of carbonyls

+ page 8 line 30 “Alfarra 2004” -> Alfarra et al. 2004

+ page 8 line 40 “No clear tendencies” -> should be trends in this context

+ page 9 line 5 “(experiments 1.2, 2.2, and 2.3)” -> should be 3.2?

+ page 9 line18f “. . .to identify and quantify the 10 carboxylic acids which are regarded as some of the most important in α-pinene derived SOA. . .” This sentence does not work. Most important what? Constituents?

+ Fig 4: Are the legend descriptions of Exp3.2&3.3 switched?

+ Fig 4: The black stroke around dark blue triangles is very hard to see -> use lighter color for -15 °C experiment (same issue in Fig 6).

+ Fig 4b: Do not put the yellow arrow on top of blue triangles

+ Fig 5: You use Kelvin as temperature unit while the text and labels use °C. -> Choose one unit.

+ Fig 5: The yellow dashed line is hidden by blue diamonds -> adjust y scale a bit to make it visible.

+ Fig 6b: where are the Exp3.1 data points? I only see red triangles with black border.

+ Fig 7 The term AMS m/z 44 *[factor] is a little bit confusing as the text speaks of (PMF) factors. maybe change this to [correction factor] or [scaling factor]

+ all SI Fig with PMF results: y axis is mass concentration not Mass. That is “lab-slang”. You can easily avoid too long y axis label by introducing an abbreviation for

mass concentration (e.g. cm or corg).

+ all SI Fig with PMF results: experiment labels are 1-8 which is different from main text -> adjust labels.

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