

Reply to review by Anonymous Referee #1

We thank the reviewer for the constructive comments, which we have addressed in a point-by-point fashion below (responses written in italics). We have modified the manuscript accordingly.

Summary

This paper investigates the effects of temperature and alpha-pinene concentration on the chemical composition of SOA particles formed via dark ozonolysis in a series of chamber studies. Experiments were performed in the dark at two concentrations, 10 ppb and 50 ppb, in the presence of ozone. Three constant temperatures were analyzed (20, 0, and -15 C), and several temperature ramps were induced at various points during the ozonolysis. Chemical composition was investigated in real-time using an HR-ToF-AMS, and offline chemical composition of filter samples was performed via LC-MS. The authors apply PMF to the AMS data in order to determine controlling factors behind the chemical composition. They discuss a four-factor solution, where two of the factors correspond to temperature and two factors correspond to alpha-pinene concentration. The authors argue that the temperature at which particles initially form is more important for determining particle composition than changes in temperature after the initial formation. However, they do find that temperature ramps lead to slight changes in oxidation levels.

The authors also compare AMS derived estimates of organic acid content to off-line LC-MS analysis of filters and find good agreement. They conclude that high temperatures and low initial alpha-pinene concentrations are associated with more oxidized SOA.

General Comments

This paper is not suitable for publication in its present form. In general, a more rigorous and thorough discussion of results with consideration of context would be helpful. There is a tendency in this manuscript to state results and not interpret them.

I also take issue with some of the findings. The second to last sentence of this manuscript is “This work confirms that the particle chemical composition is dependent on precursor concentration and particle mass loading.” This is not explored in the manuscript.

Based on the reviewer’s comments we have modified the manuscript in several places with focus on a more clear and thorough discussion of the results. Moreover, we would like to specify that a deeper discussion of some of the results can be found in the companion paper by Kristensen et al. 2020.

Regarding the second last sentence we agree that this is not explored in the manuscript - what we wanted to write is precursor concentration and temperature. This is now corrected in the manuscript: “The companion paper also shows and discusses how increased VOC precursor concentration leads to a higher SOA particle mass loading consistent with findings in previous chamber studies (Kristensen et al. 2020).

The authors state that “Factor 1” is a temperature factor, however this does not seem to be the case. Comparing experiment 1.4 to 3.1 (same constant temperature) Factor1 appears to change more than a factor of 10 for a factor of 5 change in precursor VOC concentration.

Further, Factor 1 does not change during the lower VOC (10ppb) temperature ramp experiments. Factor 1 is essentially the same for experiments 1.4 vs.1.5, though this is a little hard to discern because the y-axes are different.

Thanks for pointing out that it was not clear in the text why we refer to Factor 1 as a temperature factor. It is important to notice, that we do not compare absolute contributions of the factors but rather their relative contributions to the total mass. For comparison of experiments 1.4 and 1.5 it is the relative contribution of Factor 1 to total mass that should be compared. We see a relatively higher contribution from the high temperature factor (1) in experiment 1.4 and a relatively higher contribution from the low temperature factor (4) in experiment 1.5. Additionally, by comparing the warm experiments (1.1 and 3.1, both 20 °C but different VOC concentration) it shows that Factor 1 contributes significantly to the total mass in both experiments - and in the corresponding cold experiments (1.3 and 3.3, both 20 °C but different VOC concentration) Factor 1 is almost non-existing. We have modified the text to make this more clear, e.g. we have made the following paragraph more clear:

"According to their appearance and relative contribution to total SOA mass Factors 1 and 4 will in the following discussion be referred to as "temperature factors" and Factors 2 and 3 will be referred to as "concentration factors". For example, according to Figures 2 and 3, at both α -pinene concentrations Factor 1 makes up a significant fraction of the particle mass in the 20 °C experiments but plays a minor role in the colder experiments and therefore Factor 1 will be referred to as "high temperature factor" in this manuscript. The significant contribution of Factor 1 to the SOA mass at high temperature is in agreement with the fact that this factor is mostly dominated by ions from oxidized species (i.e. high intensity of CHO and CHOgt1 ion groups at m/z 28, 29, 43, 44, 55, and 83). Among all factors, Factor 1 has the highest O:C ratio (0.56), OSC (-0.53), f43 (14 %), and f44 (9 %) and therefore the chemical species represented by Factor 1 (i.e. related to high temperature) are likely the most oxidized and least volatile (c^) entities present in the SOA."*

The authors admit that a five- or six-factor solution provides a better explanation for the data than the four-factor solution presented in the manuscript, but do not adequately explore why the higher-order factor solutions are discarded.

The larger number of factors are not selected because they do not provide any more interpretable information about the composition. This is now explained more detailed in the Supplementary Information of the revised manuscript.

Ramp start-to-end RH is presented in Table 1, but it is not explored in the manuscript. RH values change drastically during the temperature ramp, but this information is not used in the analysis. Is it possible that the ignored factors from the PMF solution are instead factors relating to RH? If so, they should be included in the analysis and their importance should be discussed, or a more adequate reason for discarding them should be addressed.

In the PMF analysis we include only temperature ramps performed early in the experiments (i.e. 1.4 and 1.5): the largest variation in relative humidity is observed in experiment 1.4 where relative humidity changes from ~1 to ~30 % during the ramp (cooling). That is, all experiments included in the PMF analysis is conducted at low (<30 %) relative humidity. If a factor was related to relative humidity we would expect this factor to appear during temperature ramping to low temperature (experiment 1.4) and with time in the high concentration experiment as the RH increases slightly during these experiment. We do not observe the appearance of such a factor in neither the four, five, or six factor solutions.

Atmospheric Chemistry and Physics is an applied journal and it surprises me the authors provide no atmospherically relevant context for the selected temperatures, initial hydrocarbon concentrations, etc.

We agree with the reviewer that such information is lacking. We have added the following text at the end of the introduction: “The ACCHA campaign focuses on temperatures from 20°C to - 15°C representing conditions relevant in the boreal forest regions (Portillo-Estrada et al. 2013) and at atmospheric relevant concentrations of α -pinene ranging from 10 ppb, representing the higher concentrations in boreal forest (Kourtchev et al. 2016), to 50 ppb.

The authors state early in their manuscript that oxidation levels of SOA from α -pinene ozonolysis decrease with increased particle mass loadings. The authors’ findings do not seem to be consistent with this. Why?

We assume the reviewer refer to our discussion of the absorptive partitioning framework which shows that higher particle mass loading can serve as a driver of condensation of more volatile less oxidized species to the condensed phase. According to the Clausius Clapeyron equation vapor pressure is expected to decrease with decreasing temperature and would thus be expected to lead to condensation of less oxidized compounds to the condensed phase. This is actually, what we observe. To make this more clear we have revised the text to read: “In accordance with expectations based on the absorptive equilibrium framework (1), previous work (Shilling et al. 2009), and observations from the PMF analysis SOA formed from low α -pinene concentration (10 ppb) and higher temperature are associated with higher O:C ratios compared to SOA formed from the high α -pinene concentration (50 ppb) at lower temperatures. The plot shows that the SOA consists of less oxidized compounds in experiments conducted at low temperature and high α -pinene concentration, compared to high temperature and low α -pinene concentration.”

Specific comments and line numbers follow:

Page 2, Line 6: SOA is also formed through the uptake of water-soluble organic gases into condensed-phase water.

Based on this comment from the reviewer we have modified the sentence and it now reads: “Due to their low vapor pressures, some of the gas phase oxidation products may partition onto already existing particles by condensation or reactive uptake and contribute to particle growth.” (Hallquist et al. 2009)

Page 2, Line 7: The 1995 Guenther manuscript describing a biogenic emissions model is not the right reference for “SOA forms from biogenic and anthropogenic precursors”.

We agree, and we have replaced this reference with a more general reference namely the text book by Seinfeld and Pandis.

Page 2, Line 10: Hydroxyl radical (OH) should have a dot, not a minus sign.

Thanks, corrected.

Page 3, Line 28-32: Why were different precursor concentrations chosen for the temperature-ramp experiments? If precursor concentration is playing an important role in chemical

composition, then why aren't all the temperature-ramp experiments performed using the same initial alpha-pinene concentration? Here, some are done with 10 ppb and some with 50 ppb. Why are these conditions relevant?

In the revised manuscript we have only included the two 10 ppb α -pinene temperature ramps (1.4 and 1.5) initiated around 35 minutes after starting the experiment (see also reply to reviewer 2). As now stated in the introduction, a concentration of 10 ppb corresponds to the level which can appear in boreal forests.

Page 4, Line 36 – Page 5, Line 1: According to Table 1, these experiments also saw a wide range of RH, which could lead to the condensation of water onto the particles and subsequent aqueous-phase reactions. Is it possible that Factors 5 and 6 are related to RH? If so, please address this in the manuscript, or provide a justification for why these factors and the large range of RH values can be ignored.

The ramps with a large change in relative humidity have been omitted from the manuscript (see also answer to reviewer 2). In all experiments included in the PMF analysis $RH < 30\%$.

Page 5, starting at Line 14: The authors state, "Under all conditions (i.e. in all experiments), the AMS derived SOA densities are in the range of 1.1 to 1.3 g cm⁻³. Figure 1 indicates that SOA density is < 1.1 for the first 0.5 hour.

The sentence has been modified to:

"The AMS derived SOA densities at mass peak are of the order of 1.1- 1.3 g cm⁻³. Figure S9 suggests a slight increase in density with higher experimental temperature as well as a slightly higher density for the particles formed at low α -pinene concentration (10 ppb) compared to high α -pinene concentration (50 ppb)."

See also reply to comment below in relation to SOA density.

Page 5, Line 32-35: Please provide a reasoning for using only some of the temperature ramp experiments in the PMF analysis.

We have re-considered the ramp experiments conducted at 50 ppb α -pinene and decided to omit these three ramps from the analysis. The main reason is that these ramps were performed after filter sampling for the off-line analysis. Filter sampling results in significant reduction in the chamber volume in a short time, which means that conditions in the chamber are different after filter sampling.

PMF analysis was conducted on experimental data during the first up to ~250 minutes of the experiments. Therefore, the two 10 ppb α -pinene ramp experiments, where the temperature ramp was started ~35 minutes after SOA formation and completed after ~160 min, are included in the PMF analysis.

Page 6, Line 29-30: What contributions from f44 and m/z ratios do Factors 5 and 6 have?

As now explained in the Supplementary Information the 5- and 6-factor solutions do not provide additional information and we therefore focus the analysis on f44 and m/z ratios from the 4-factor solution only.

Page 7, Line 12-14: Please provide a discussion regarding why it makes sense to have less-oxidized SOA at low temperatures and high alpha-pinene concentrations. It is interesting that

this is the case, but a scientific justification is missing and should be discussed. Is this a matter of kinetics and competition for oxidants?

See answer to comments above and relation to partitioning considerations.

Page 7, Line 31: Why is no OH scavenger used, and how does potentially changing [OH] confound interpretation of O:C ratios and factors? The authors provide some speculation on Page 7, but the context is insufficient.

An OH-scavenger can be added to chamber experiments to study ozonolysis reactions in isolation while experiments without scavenger are generally considered more realistic although also more complex. The ACCHA campaign was conducted without use of OH-scavenger so that both ozone and OH-radicals acted as oxidizing agents during the course of the experiments. The ratio between oxidation by OH- radicals and O₃ was modelled in selected experiments using the master chemical mechanism v3.3.1. It was found that the ratio of VOC oxidized by O₃ relative to that oxidized by OH-radicals was ~2:1 independent of temperature and precursor concentration (Quéléver et al. 2019). This is now mentioned explicitly in the text:

“Modelling suggests, however, that the OH oxidation is not more pronounced at low temperature (0 °C) compared to high temperature (20 °C) (Quéléver et al., 2019), which makes this a less likely explanation for the continuous increase in the O:C ratio and H:C ratio in the cold experiments. More specifically, the ratio of VOC oxidized by O₃ relative to that oxidized by OH-radicals was ~2:1 independent of precursor concentration and temperature.”

Page 8, Line 18-24: A lot of time and energy is spent on discussing the reasons behind changes in the O:C and H:C ratios during temperature ramps in previous paragraphs. However, here it is stated that the changes are small and not very important. If that is the case, then why discuss the changes to the O:C and H:C ratios so extensively? It seems this section could be more focused.

There are some changes in O:C and H:C ratios during the temperature ramping and we find it justified to discuss it. At the same time, it is also true that the changes are small compared to the differences between particles formed at different temperatures. To make this more clear we have modified the text in this section.

Page 8, Line 39 – Page 9, Line 9: Please provide a reasoning for why a lower precursor concentration leads to more highly oxidized SOA. Is this because there is less competition for oxidants?

Lower precursor concentration means less particle mass and thus it is only the more oxidized species that have low enough vapor pressure to condense, see discussion on partitioning framework above. We have added a reasoning in the text as requested by the reviewer (only bold text):

“This suggests that acid-derived functionalities are more prevalent in α -pinene SOA formed at low precursor concentration (and thus low particle mass loading) which is consistent with less partitioning of the more volatile, less oxidized compounds to the particle phase.”

Page 10, Line 9-12: The authors state that organic acids with heavier backbones are formed at lower temperatures. Why does this make sense? Is this due to volatility reasons?

The finding is consistent with the lower O:C ratio at lower temperature as reported by Kristensen et al. 2017 in the AURA chamber and recently also reported in studies from the CLOUD chamber at CERN (Simon et al. ACP 2020). This trend is attributed to the effect of temperature on peroxy radical chemistry.

Figures and Tables: Table 1: Do I understand correctly that no experiment was repeated and there is no demonstrated repeatability?

The ACCHA campaign was carefully designed with repeatability checks in mind. For reproducibility with respect to time evolution of SOA mass, α -pinene concentration, O_3 concentration, temperature and relative humidity see supplementary material in Kristensen et al. 2020.

The following text has been added to the manuscript:

“For reproducibility with respect to formation of SOA mass as well as loss rates of α -pinene and O_3 see Kristensen et al. (2020).”

Figure 1: Particle density is presented with four significant digits and no estimate of uncertainty. There should be uncertainty bars or some other representation.

We agree that four significant digits is too much. We have removed the density in Figure 1a.

Figure 4: In panel b, what is the black line? It is not labeled.

The black line is the same as in panel b, but it should be noted that the scales on the axes are different. To make this more clear, the caption has been modified adding:

“Notice the different scales of the axes in panels a and b.”

Figure 6: In panel b, the black line is not defined. Why is the black line in panel b different from panel a, if they are both based on Heald and Ng?

The black lines are the same - it is the scales on the axes that are different in panels a and b. To make this more clear, the caption has been modified adding:

“Notice the different scales of the axes in panels a and b.”

In panel a, it is unclear how this figure supports the author's conclusions regarding the oxidation level of SOA in each experiment.

Panel a) is included to show where the results from this work fall in relation to the lines suggested by Heald et al. (2010) and Ng et al. (2011). If the axes in panel b has been changed to allow for inclusion of both of these lines the detailed information about time evolution would be lost.

Supplemental Information: Figures S5 and S7. Could these extra factors be attributable to RH? They seem to play a consequential role in mass loading

This question has already been answered in a former question.

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