Review of Muntzel et al. 2020 “Importance of SOA formation of a-pinene, limonene and m-cresol comparing day- and night-time radical chemistry”

Summary

The authors present a study about the SOA formation potential of three precursors that are relevant for the ambient atmosphere. They compare the SOA mass yield and SOA particle composition for two different formation pathways – reaction with OH radicals (representing daytime photochemistry) and reaction with NO3 radicals (nighttime chemistry) – while also investigating the impact of different humidity regimes. As there is limited data available especially for the NO3 radical chemistry, this is an important investigation which will help to improve the understanding of SOA formation processes from a range of different precursors and oxidants.

However, certain issues have to be address prior to publication in ACP. The main problem lies with the still unclear presentation of the work. Several pieces of basic information are either not stated clearly or left to be guessed by the reader (see below for examples).

Major Comments

1) There is no information about the VOC and NOx concentrations. Concentrations (or even better exposure values) for NO3 and OH radicals are also missing. This makes it very difficult to relate this work to the existing literature. Even if these values may be stated in a previous paper about this data set, it is not acceptable to ask the reader to search for this vital information. At least the starting VOC and average NOx concentration must be stated (e.g. added to Table 1). At least an estimate of the OH and NO3 exposure must be given. What does 90 min of reaction time in the chamber represent? Is it equivalent to an average day/night of reactions at ambient conditions? Or is the exposure much greater.
2) The authors do not explain how the yield values were calculated. It may seem trivial to them, but it is important to be stated. Also, it has to be clarified that each yield curve in Fig 1 stems from a single chamber experiment and thus represents the evolution in reaction time as well as in formed organic mass space.
3) One key finding of this study is the difference in SOA mass yield. It is commendable that the authors present the yield vs organic mass curves (Fig 1) and then use the approach from Odum et al. to take their shape into account. But when the overall yields are compared between the precursors, the authors do not clearly state that now they are comparing the yields at the end of their 90 min chamber experiment. By doing this, they completely ignore the different turnover in their experiments (i.e. how much of the VOC reacted). The overall interpretation should not change. But if the experiments are compared for the same ΔM value, the detailed interpretation may differ. As an example, for the 75%

RH case, cresol+OH has a higher yield at ΔM=10 ug m^{-3} than limponene+OH. Guessing that the same initial VOC concentration was used in both experiments, this behaviour should yield information about differences in reaction rates for the two precursors. This is of interest as there is so limited data about these reactions. For future studies, it may be advisable to also conduct experiments with higher initial VOC concentration to compensate for a slower reaction rate. For the manuscript I request that the authors clearly state that they compare the yield ($t_{reaction}$=90min).

4) The authors compare their yields after 90 min reaction time of an unknown amount of VOC with an unknown amount of OH or NO3 radicals to the yield values measured in other studies. As they clearly show in their Fig 1, the SOA mass yields are highly dependent on the reaction time or the formed organic mass. How comparable are all these values in the literature to your experiment settings? Did you only compare literature values with comparable ΔM? Or did you base the comparability on the reaction time? Or the VOC turnover (ΔVOC)? Or the exposure to OH/NO3? Please clarify how you selected the studies and if necessary adjust the examples selected in the manuscript.

5) Similar to a previous reviewer, I wonder why the authors call cresol SOA “anthropogenic” if its main source is biomass burning which is not generally considered “anthropogenic”. I am not satisfied with the reply to the previous reviewers comment. Just because cresol is an aromatic compound does not automatically mean it stems from an anthropogenic source as is typically assumed for benzene or toluene. Additionally, the connection of cresol to biomass burning is not mentioned in the introduction but only at the end of section 3.3. The authors need to shift this information to the introduction and clearly state that while a-pinene and limonene are biogenic VOC, cresol is a VOC mostly connected to biomass burning. The term “anthropogenic” should be replaced by something more fitting (e.g. aromatic).

6) The SOA-bound peroxides value for the dry a-pinene+OH experiments seems extremely high and such a value would have important implications for the interpretation of many measurements. The authors speculation for the reasons for that seem plausible. However, I assume the authors did not conduct any repetitions of the chamber experiments (as it is very time consuming). Your interpretation is then based on a single filter sample from a single experiment. How reliable is that? I.e., is it possible that “something went wrong” in collecting and handling the filter or during the peroxide measurement?

7) The overall language needs polishing in a lot of places and would benefit from the input of a native English speaker. The structure of many sentences is closer to German than to English which makes the manuscript difficult to follow. Overall, the language style is inconsistent and gives the manuscript a “sloppy” character (see specific comments for examples). This has been noted by previous reviewers and – in my opinion – has not improved since the previous manuscript version.

Specific comments

+ In several places, acronyms/abbreviations are not properly introduced (e.g. BSOA in line 66, QF filter in line 92, or HMWC in line 422 to name just a few). The authors must introduce all acronyms/abbreviations and then use the introduced terms in the following.

+ The use of "day-time", "day time" and "daytime" is not consistent within the manuscript. According to the online Cambridge dictionary and Merriam-Webster the noun should be "daytime" (and nighttime, respectively). ACP may have a different preference, but in any case, chose one spelling and stick with it.

+ The term "the present study" should be replaced with "this study" as it is much more reader friendly. In the context of this manuscript, it is always clear that the authors are referring to their own work. However, the ACP style guide may differ from my opinion.

+ The term "under RH" is used several times. It should be "at elevated RH" or "under higher RH condition".

+ The authors switch between VOC+NO3 and VOC/NO3 for their experiment labels. Decide which you like and stick with it.

+ L 22ff: The statement that the SOA formation potential of limonene with NO3 significantly exceeds that of the reaction with OH is only strictly true for the dry case and when comparing the $t_{reaction}$=90min points. For 50% and 75% RH this is not correct. The yields are comparable or even higher for OH. The authors need to correct this statement.

+ L 44: BVOCS acronym not introduced

+ L 51ff: this sentence is difficult to understand. Rephrase to make clear what is causing what.

+ L 53ff: The structure of the sentence is very difficult to follow. (paraphrasing: "The reaction is suggested to be more important for BVOCs than AVOC being the reason…" rephrase.

+ L53ff: Here is the first time the authors bring up biogenic vs anthropogenic VOC when discussing the different chemical reaction behaviour. In this respect, the main important functionality in the compounds is the aromaticity of many anthropogenic VOCs. Considering cresol being a biomass burning tracer and not necessarily a true anthropogenic VOC, "anthropogenic" should be changed to "aromatic" to highlight that this is the real reason for the different chemical behaviour. (Also adjust the label in L 72.)

+ The chamber description in section 2.1 is missing some important details. Yes the previous paper contains these details, but the following basic information needs to be directly available to the reader of this paper:

- It is not clearly stated if the chamber is operated in "batch mode" or "flow through". Is the removed sample volume replenished or does the chamber change size?
- What is the material of the chamber?
- Were the particles dried prior to injection? Are they in liquid or solid phase state when equilibrating to the RH inside the chamber?

+ L 82: Is the chamber itself actively humidified or does the humidifier condition the air that is used to flush/fill it?

+ L 88: You speak of a pre-reactor, then of a flow tube. It is not clear that they are the same thing.

+ L 91: “samples were taken at filter” ? Please correct this to whatever you mean.

+ L 92: “QF filter” neither is the acronym explained nor the brand/make stated.

+ L 100: PTR-TOFMS acronym not introduced.

+ L 101: according to what?

+ L 103: You used an intermediate RH to determine particle wall losses. How representative is that for the dry experiment? dry and wet deposition may be different. Especially if the phase state of the particles changed.

+ L 106: add a comma between reaction and conditions to clarify the sentence meaning.

+ L 117: The authors replied to the previous reviewer question that they use 1.0 g cm^{-3} as particle density because the real density of the particles is not known. The way this is phrased here suggests that 1.0 g m^{-3} is the true density (2 out of 3 readers misunderstood this information). It needs to be added in the text that in absence of any reliable density estimation, 1.0 g m^{-3} is used instead.

+ L 118: was the water content accounted for when calculating the change in organic mass ΔM? I.e., was the whole volume as measured by the SMPS considered to be organic material? Or was a fraction subtracted according to the hygroscopic growth estimated for SOA at 50% and 75%?

+ L 136: why is “biogenic and anthropogenic marker compounds” an italic subheading instead of adding it to the section heading?

+ L 130: IC-CD acronym not introduced

+ L 144: HPLC acronym not introduced

+ L 156: add the purity information for the pure chemicals from commercial sources.

+ How was the yield calculated. What assumptions were made?

+ L 177: Eq. (Eq. 1) correct typo

+ L 178: it should be M_0 both times. not M

+ L179: M_0 is not listed

+ L 180: add “the” before mass yield

+ L 185: tiny tables in Fig 1. Even at 200% zoom, the numbers in the tables in Fig 1 are barely readable. Increase font size.

+ L 189: Can you really directly compare the parameters from a one product Odum fit with a two product fit? Have you tried fitting your data with a two product fit? How do the parameters compare?

+ L 200: It is not clear which of the 4 Fry et al. references is meant here.

+ L 212: “…proceeds via further reaction… “ this is an ambiguous statement. Rephrase to clarify.

+ L 213: Isn’t the limiting factor that the first-generation products are not of sufficiently low volatility to partition in the particle phase at the organic mass loading at that time? Further oxidation creates compounds of lower volatility which will contribute to particle mass. A different reaction pathway forms products with a different volatility distribution.

+ L 216: In the presence of NOx, organonitrates should also form in the OH experiments.

+ L 219 yield from limonene + NO3

+ L 220ff: 16-29% is close to 29-69%? I disagree. I also disagree with your statement that the NO3 reaction yields more SOA than ozonolysis.

+ L 224 ff: You cannot compare the importance of NO3 vs OH vs O3 without stating how your experiment conditions relate to ambient conditions (what is the equivalent OH/NO3 exposure or oxidative age?). Unrealistically high NO3 values would distort your findings. AS you do not give these values one can only wonder.

+ L 230ff: how much SOA mass was formed in your blank experiments (seed, oxidants but no VOC)? How does this “chamber background” SOA compare to the SOA mass formed in cresol+NO3?

+ L 241: “…was used.” ? was used to form OH?

+ L 249: “Aa discussed before…” N2O5 has not been mentioned anywhere before this point in this manuscript. Adjust the wording to reflect that.

+ L 253: “…- as to the authors’ knowledge…” remove the “as”

+ L 262: remove “Contrary”. This implies a connection to the previous sentence that is not there.

+ L 274:”Fig 1”? should that not be Fig 2 here?

+ L 274f: The numbers in parenthesis do not match the sentence meaning. 60 is larger than 20 but the statement is opposite.

+ L 280: change “suggested” to “assumed” or “inferred”

+ L 281ff: Why would the behaviour of endolim create a RH dependent response? nothing in your explanation suggests a RH dependency.

+ L 291ff: same as for the previous paragraph. Why does this behaviour explain the observed RH dependence?

+ Regarding the RH dependence of Cresol+NO3 SOA yields. Have you considered a process analogue to the formation of isoprene SOA? There, smaller, semi-volatile but water-soluble compounds are taken up into the particle phase where they oligomerise and for low-volatility products. An aqueous phase enhances this by drawing the water-soluble compounds from the gas phase and also catalysing the condensed-phase reactions especially if $SO4^{2-}$ ions are present (forming low volatility organosulfates).

+ L 310: Fig 7 is mentioned before figures 3-6.

+ Fig 7: MNC is -5-nitro in the caption but -6-nitro in the figure label and the main text.

+ L 315: OC and WSOC are introduced here after they have already been used earlier. Ensure that acronyms/abbreviations are written out when they first occur and use the acronym/abbreviation consistently throughout the rest of the text.

+ L 319: What is the relationship between WSOC and NPOM. It reads here (and in the methods section) as if these two names are interchangeable. Is that the case? Is WSCO derived from the NPOM measurement?

+ L 319: The authors speak of OC/EC and WSOC. But Fig 4 shows OM and NPOM. It is not explained how OM relates to OC/EC. It may seem trivial to the authors. But you cannot expect the general ACP reader to know all your measurement equipment and what quantities are measured/derived.

+ L 320ff: When comparing the SMPS derived mass values with other directly mass based measurements, it is very important that the authors state their assumptions for the density, i.e., that it is set to 1.0 g cm^{-3} and is constant for all conditions. In comparable chamber experiments particle densities of 1.2 – 1.4 g cm^{-3} are typically derived. This means that the reported ΔM(SMPS) are most likely 20 – 40% too low. This has to be at least mentioned and considered when giving the uncertainties for the SMPS (caption of Fig 4). I recommend that the authors focus more on the qualitative trends ΔM(SMPS) and OM (and NPOM, respectfully). This agreement may be an indication that the density does not change significantly with RH for these experiments.

+ Fig 4: it is not directly clear what the % values refer to. Add this information to the Figure caption.

+ Fig 4 the uncertainty regarding the particle density needs to be mentioned when stating the uncertainty for the SMPS measurement. From the current wording it is not clear if the 10% already are supposed to take the density uncertainty into account.

+ L 322: "..except mass originated from limonene" replace with "…except in the limonene experiments"

+ L 324: replace "compound" with "precursor"

+ L 325: remove"is" (… with x% of org mass composed of…)

+ L 325ff: Have the authors considered that in the limonene+NO3 case a large fraction of hydrophobic products may be produced. An aqueous phase could then hinder the uptake of these compounds (quasi reverse co-condensation) which then stay in the gas phase leading to a lower SOA mass yield. It does seem odd that this happens in the NO3 case where the authors expect a higher organonitrate content. In general, the polar nitrate groups should make the molecules more hydrophilic

+ L 326: Now the term "WSOM" is used. How does that relate to NPOM and WSOC? These inconsistencies make the manuscript hard to follow.

+ L 325ff: At least the name of the measurement principle for the peroxide measurement should be given here or better in the methods sections.

+ L 336: change "it" to "is"

+ L 337: Is the "mostly dimer" assumption still valid considering the more recent information about the highly oxygenated material (HOM, (Ehn et al., 2014)) that is produced in auto-oxidation processes. Most of these compounds contain hydroperoxide groups but are not necessarily dimers.

+ The absence of a RH dependence my be connected to the higher content of water-insoluble material in limonene SOA. If enough water insoluble material is present, a separate organic phase may form in which the peroxide compounds are "protected" from hydrolysis.

+ L 338: What is "the organic mass formed during the experiment" referring to (M_{org})? The mass as derived from the SMPS measurement? Then the same thoughts regarding the uncertainty of the particle density apply here and should be clearly stated.

+ L 365ff: It is impossible to evaluate this comparison as no NOx values are given for the experiments in this study. Terms like low/medium/high are very subjective.

+ regarding possible artefacts in the peroxide measurements: How much H2O2 is left in the chamber? H2O2 uptake into particles may play an important role if very high concentrations of H2O2 were present (e.g. ppm level). The statement “blank filter were carefully checked” is not clear. Are these the filters collected after the blank experiments? Or are these blank filters? Will the uptake of H2O2 be the same on pure (NH4)2SO4/H2SO4 particles as on mixed inoganic/organic?

+ L 393ff: It is not clear to me what the marker compounds are normalised to. The SMPS derived organic mass? Or the OM? Or the HPLC Signal?

+ L 406f: LWC and ALWC are not introduced. Is there a difference between the two quantities? Or is this another one of the inconsistencies that are spread throughout this manuscript?

+ L 422: HMWCs is not introduced.

+ L 450: state also the higher values to make the comparison with the low RH values easier.

+ L 466: The O in ROS stands for oxygen – not organic! This term refers to the species creating oxidative stress in the system. These compounds can be organic peroxides. But it is definitely not referring to all organic. Non peroxy organic aerosol also have adverse health effects but via different mechanisms.

+ L 482: The structure of the sentence “The formation of pinonic acid…” does not make sense in English. “proceed” is not the correct term when talking about chemical formation mechanisms. A phrase such as “Pinonic acid might be formed from the oxidation of pinonaldehyde that itself has been found for NO3-radical initiated reactions of a-pinene.” is much clearer and describes the ongoing processes more precisely.

+ L 491 “pointed out to be” do the authors mean “turned out to be”?

+ L 495: The reactive species in the gas phase are only a reservoir for particulate matter if the reaction products have a sufficiently low vapour pressure or if other mechanisms form low volatility materiel (e.g. particvle phase oligomerisation as in the isoprene SOA case).