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## Comment on acp-2021-1080

Anonymous Referee #1

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Referee comment on "Chamber investigation of the formation and transformation of secondary organic aerosol in mixtures of biogenic and anthropogenic volatile organic compounds" by Aristeidis Voliotis et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-1080-RC1>, 2022

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The manuscript by Voliotis and coauthors describes a set of smog chamber experiments, in which the authors study the formation of secondary organic aerosol (SOA). Both individual precursor volatile organic compounds (VOCs), and their binary and ternary mixtures are studied. As such, the topic is timely and relevant for the scope of the journal. The majority of existing literature focuses on single VOC systems, or to a smaller extent binary mixtures. As a result a large proportion of the manuscript, and its relevance, comes from the design and analysis of the ternary mixture of precursors. In this aspect, AMT might be a suitable journal as well. However, I think there is substantial enough scientific evidence as well for consideration for ACP. The experiments are for the most part comprehensively described and analysed, with references to companion papers under preparation as necessary. All in all, the manuscript details a large body of work and analysis, and for this the authors are to be commended.

The strength of the manuscript, namely its broad and comprehensive scope, is also one of its weaknesses. The manuscript is long, and at times hard to follow. Some restructuring may benefit its readability, and thus make the results more accessible to the scientific community. I have listed some specific suggestions below.

Major comments related to the structure of the manuscript:

- It took me quite long and a lot of guessing to figure out the experimental procedure, including the generation of oxidants. The method for the OH radical generation is only revealed in the beginning of the results section. This would be very relevant already two sections before, in the "experimental design". Also, the separation between "experimental design" and "methodology" is not always very clear to me. I would have a thorough look at sections 2 -- 4, and try to ensure that they are logically structured. This would greatly help the reader in understanding what was actually done. For example, the seed generation is described in detail already in section 2.2, while the generation of oxidants, in

my opinion much more important part, only comes way later in the results, as mentioned above.

- I have similar concerns with the results and discussion sections. Quite a few new results or analyses are introduced in the discussion, where no new results should be presented. As an example of this is the mention of the different time trends in lines 846-848. Although this was already seen in a figure in the results section, there was no real mention of it in the text, let alone of explaining it in terms of different isomers. Try to introduce all the results in the results section, and reserve the discussion section for the discussion of results already introduced before

- For a long time I thought that this is the first paper to be published on these experiments. Only towards the end of the results section was Voliotis et al., 2021a cited. It would be very important to make it clear already early on that something has already been published.

- Related to the previous point: currently the manuscript contains a lot of results. Quite a large fraction is also left out of this manuscript as their own papers, which is good. Would it be possible to omit some more of the results from this manuscript, and move them to the more specific papers? It could improve the readability of this manuscript. For example, the top three panels in Fig. 11 are essentially identical to the bottom panels in Fig. 1 of Voliotis et al., 2021a.

- Figure captions are often very brief and lack essential information. These should be fixed.

- Data availability: I would personally like to see a more open data policy, with the data readily available in some public repository. I understand that this may be a challenge, but if possible, it would be good to move towards more open data policies.

- In many parts of the manuscript, I feel like things are being said in a needlessly complicated and jargon-filled manner. This is not necessary to convince readers. On the contrary. You already have a fine set of experiments and analysis, now it would be good to help the readers get the most out of it by being extra clear.

Specific scientific comments:

- Have you quantified the first order wall loss rate of non-volatile vapours in the chamber? It would be useful to compare that to the condensation sink caused by the particles in the chamber. I think the seed concentrations sound high enough to be the main sink, but it

might be good to verify. The total aerosol loading varies a lot between the experiments, so the condensation sink also varies. This could mean that in the low SOA cases the walls are more important than in the high SOA cases. The same also applies to the partitioning behaviour: it would be good to comment on these.

- There is quite a bit of discussion on whether isoprene should be included in the predicted SOA yields. However, as far as I understand it, it makes no difference. Example: Let's say that  $\alpha$ -pinene has a SOA mass yield of 0.1, and isoprene of 0. Then, if you oxidize 100 units of AP and 100 units of isoprene. The predicted yield for the whole mixture is  $(100 \cdot 0.1 + 100 \cdot 0) / 200 = 0.05$ . Excluding isoprene it would just be 0.1. Predicted mass, in the first case, would be  $0.05 \cdot 200 = 10$ , while in the second case (again excluding isoprene) it would be  $0.1 \cdot 100 = 10$ . So the same result. Thus, it does not make a difference in the linear prediction whether you exclude or include a zero yield component. Or am I missing something here?

- For me, the most important figure is Fig. 5, where you compare the predicted and measured yields. However, this figure is relatively hard to read. It would be important to make it more legible. Also, in many occasions you compare the modelled yield to the measured one. For example, line 507: "predicted yield... is higher than that measured". I think the more logical comparison would be vice versa: "Measured yield is smaller than predicted". This would directly tell of any enhancement or suppression.

- The information in Fig. 5 and table 4 would be nice to have in some sort of easily digestible graphical form, where you would easily see if the measured yield is a) smaller than b) roughly the same as or c) greater than that predicted by individual yields.

- In many parts of the manuscript, the authors discuss rates of change in different contexts. In many, if not all, cases, I don't think the rates (=time derivatives) are themselves relevant. E.g. high SOA concentration is more important than high SOA formation rate. See my line by line comments for more details.

A list of individual comments related to the content

- Line 21: mention already in the abstract that this is a chamber study

- Line 21: iso-reactivity. I don't believe this is a standard concept, at least I was not familiar with it. Remove from abstract, or explain better, and definitely explain better in the main text. Especially if it is your own definition

- Line 22: "assumed dominant oxidant". For the most part, you calculated that it indeed is the dominant oxidant (with the notable exception of  $\alpha$ -pinene). "assumed" sounds too uncertain and vague.

- line 44-45: add a very brief description of what SOA is
- Lines 47-48 photochemistry dictates SOA fraction of PM: precursor emissions are very important in dictating this, and I wouldn't count them as photochemistry. Also dark chemistry plays a role. So I think "dictates" is too strongly said
- Lines 60-61: "SOA formation is considered less mechanistically": is this so? Please add reference
- Lines 76-77: add reference
- Line 79: "OH controlled by isoprene": Berndt et al also provide another (possibly more plausible) mechanism: would be good to mention it already here
- Line 79-81: I think Berndt et al have very similar conclusion, so would be good to cite them as well
- Line 85: both ethylene and isoprene
- Lines 97-98 Add reference
- Line 102: doesn't the Bianchi et al HOM definition only include autoxidation?
- Lines 154-156: Are you using these arguments or not?
- Line 168: "in particular": I don't think sesquiterpenes are an important enough example to count as "in particular". More like "as an example". Or then change to "some (poly)unsaturated compounds, such as sesquiterpenes" etc. Also, a reference would be good
- Line 171-172: you just said that reactivities vary, so similar concentrations are more of an exception than a rule, right?
- Line 174: "SOA particle formation potential": should you just refer to this as the mass yield? As it is mass yield you are talking about later
- Lines 179-180: "arbitrarily selected definition": you should at least give some small teaser as to what you mean, the reader can't be expected to be jumping back and forth all the time
- Line 197-198: "Nucleation and its attendant stochastic elements": feels like this is said in an unnecessarily complicated way. Do you mean that the system will be less sensitive to small changes in temperature, impurities etc.? I don't think there's anything inherently stochastic in nucleation itself
- Line 199: "earlier formation of SOA mass": I would rather say higher, as it enables larger fraction of condensible compounds to go to particles, as opposed to walls. Esp. in batch mode this also translated to higher overall mass
- Lines 204-205: it is well acknowledged that inorganic seed behaves differently from organic. I would actually stress this point even more, as the amount of SOA formed differs greatly between systems. So while in the a-pinene oxidation case, the particles are almost entirely organic, in some other experiments there may be only a thin coat. This may have implications to the partitioning of semivolatiles.
- Line 206-207: this implicit assumption may not hold, see previous comment

- Lines 204-207: again a very long sentence, better break in pieces.
- Lines 207-208: does this mean that the chamber is especially dirty with respect to NH<sub>3</sub>? Does this have any other implications
- Seed generation in general: are the seed particles dried or not? So are they effloresced or deliquesced?
- Line 209: supposedly also potential saturation at high signals? And what do you refer to with the "sampling requirements"?
- Lines 211-212: what is the relevance of mentioning single particle detection and ensemble measurement here? Both can have high or low detection limits (and also saturation at high signals)
- Line 220: the fact that the chamber is teflon should be mentioned already earlier
- Line 221: so are they a challenge or not? "modest challenge" sounds like yes, but "unnoticeable" sounds like no
- Line 223: "simulated solar spectrum" do you have a reference for this?
- Line 225: do you have a quantification of the vapour wall loss? Can you present a comparison to condensation sink? What is "sufficiently large"?
- Line 244: Is this the same for all compounds? o-cresol is (almost) always reported to the 100 ppb, while AP is reported to the ppb. Also, exactly same concentrations on successive experiments? Is it only one measurement of the VOC concentration? Or are these calculated concentrations? Something doesn't quite match here
- Lines 250-251: most of the work is on different single and binary systems, but here you only mention the single ternary system
- Line 256: what does isoreactivity mean? Is this a concept defined by you? If yes, you should make it very clear
- Line 257: so is this purely calculated ratio, not measured? But it is presented as a measurement result in table 1?
- Lines 260-261: values for which precursor? Also, give reference
- Line 266: what are the others? Again, help the reader a bit more. What about nitrate radical?
- Lines 267-268: again, I think it may be good to move the experimental section before this. Now I'm constantly getting these little nuggets suggesting how the experiment is conducted, and having to try to figure it out myself. How was OH produced?
- Line 272: OH from ozone photolysis? How exactly does the NO+HO<sub>2</sub> flux relate to this? Isn't that a sink for HO<sub>x</sub>? A schematic figure, or at least a through explanation on this, would be good
- Line 275: "rate of oxidation will be slowed": Of course, if you reduce the precursor concentration. But did you try to quantify the oxidation rate?
- Line 276 How is the ambient OH reactivity relevant here? And its measurement

methods?

- Line 278: did you measure this?
- Lines 279-280: why would it be desirable? For atmospheric relevance? Then explicitly mention this
- Lines 284-285: Give reference
- Lines 285-286: Good point, a common feature in chambers. Reference?
- Line 303: inlet to the chamber?
- Line 311: as gaseous contaminants, I would be more concerned of organics than NO<sub>x</sub> and O<sub>3</sub>
- Lines 321-322: particles are not size selected? Maybe mention this
- Line 357: actinometry and off-gassing experiments: please give more details
- Lines 362-364: this should be mentioned way before
- Lines 376-378: this should be mentioned in the caption as well
- Line 380/Fig 1.: Why does the NO not start at zero? Also, should not the initial NO and O<sub>3</sub> slopes be the same? If something, I would imagine NO to be shorter lived, so its slope should be smaller than that of O<sub>3</sub>. Now only the d-panel looks like this, and even there the NO concentration starts at a high level.
- Fig 1.: In the a-pinene/isoprene case, why is the NO so low compared to either single case?
- Lines 407&413/Fig. 2: is standard deviation a relevant number for such a small number of experiments?
- Lines 416-417: add reference
- Line 420: in none of the experiments was all of the VOC consumed. Only in a-pinene experiments was there more than half consumed. This is very far from "not all VOC was consumed in all experiments"
- Line 421/Fig. 3: particle mass peaking in o-cresol experiments is hard to see in the plot. Maybe separate into subplots?
- Line 433. This paragraph discusses a figure in the supple. Could the whole paragraph be moved to the supple?
- Line 462: what are the data points? There are 27 (?) for o-cresol, even though there were only 4 experiments. So multiple data points per experiment? This should be pointed out
- Line 491: hypothetical particle mass
- Line 496/Fig5: I think this is the most important figure of the paper, but it is pretty hard to read

- Line 504-505: How is this "indeed"?
- Lines 507-509: see my comments about including isoprene in the yield calculations above
- Lines 519-521/Table 4: I think this (or something similar) would be nice in a graphical form. As I understand it, we are interested to see if the measured yields are a) higher, b) same or c) lower than the prediction as a linear combination of yields from single precursor experiments. A plot where you can clearly see this would be very useful
- Lines 546-547: please compare both the same way, i.e. ozone compared to OH for both, or then vice versa
- Line 554/Fig. 7: Expand caption, now this tells very little. This is a common problem with other captions as well
- Line 567: "the reverse is true": what is the implication?
- Line 570-571: Makes sense. Though they are pretty different chemically also otherwise, not only in carbon number
- Line 587/Fig.8: Again, more info in caption. Like that this is particle phase
- Lines 594-595: Why does the negative mode show predominantly o-cresol derived products, but positive a-pinene derived?
- Line 595: was retention time used in the identification as well?
- Line 596/Fig 9: change the panel order to a-->b-->c-->d
- Line 599, also elsewhere: spell out -ve and +ve
- Line 605/Fig. 9: misleading labelling: a-pinene doesn't refer to a-pinene, but to compounds, which were detected in single a-pinene experiments. Or more precisely, that have a formula that was detected
- Lines 609-610: the sentence is hard to follow.
- Lines 612-613: Are there any real differences between experiments?
- Line 614: mention that this is particle phase
- Line 618/Fig. 10: what is the normalized peak area? Are we presented isomeric fractions, or fractions of the total signal? Is the normalization the same in LC-MS and FIGAERO? If yes, then why does FIGAERO vary much more? In the last FIGAERO desorption, o-cresol system has at least 4 x higher signal compared to any other, while lc-ms is more or less the same for all systems. Can we get non-normalized data? Isn't the last FIGAERO desorption the most direct comparison to the LC-MS? Also, o-cresol FIGAERO time trace looks suspicious: why such a dramatic increase after three and a half hours?
- Line 625: change showing to implying etc.
- Line 636: Voliotis et al., 2021a had two methods for volatility calculation. Why was only one used here? Also, a, however brief, explanation of the calculation would be useful here as well

- Line 637: Would be very important to mention already before that something has already been published on these experiments (?). For example, Fig. 11 top panels are essentially identical to Voliotis et al., 2021a Fig. 1 bottom panels? Up to this point (more than half way), I thought that this was the first publication
- Line 641: these cannot be found, at least not yet
- Line 644/Fig 12.: these volatility distributions seem very narrow, with a very large fraction (around 80 %) in just a single bin. I feel that this is a common feature in FIGAERO measurements, but one that must be some kind of an artefact. A discussion on this would be very welcome. Now it just feels like the figure is giving me the finger
- Line 648: what does "differences in evolution of the SOA particle components" mean?
- Line 649: you talk about all systems, but only show three. Why?
- Line 651: rearrange these to match the figure. Also, what is presented is kappa, not hygroscopic growth factor?
- Line 651: "indicative of their phase state": give more details. Not evident for the general reader
- Line 654-655: "it is clear that the rate of change": not to me, I don't see anything dependent on the rate of change here. Would anything be different if the changes were to happen over 12 hours, instead of 6? Instead, it is the particle composition that is the driver
- Line 659/Fig. 13. The figure does not show any rates, but mass fractions. Similar confusion happens also in other points of the manuscript
- Line 661: "increasingly rapid transition" does this mean with respect to time in a single experiment, or going from left to right panel? Might be again useful to break the sentence into parts. Also, would it be possible to plot the middle row with time in the x-axis, as is done with the top and bottom rows?
- Line 662: More explanations on the kappa (and other stuff in the caption as well). To the general reader the legend (HTDMA with different size classes, CCN) may not mean anything. Also, I suppose that the particles didn't grow enough in the isoprene-o-cresol-case to have the HTDMA data at 200 nm, but this is something that should be explicitly mentioned.
- Line 671: not only "can lead", but "does lead"
- Line 678: more ozone production, or higher ozone concentration?
- Line 682: what is the meaning of the low phi values?
- Line 683: Throughout, the term turnover is used. Maybe use oxidation rate instead? I find turnover slightly confusing in this context
- Lines 688-689: If we trust the numbers, O3 in a-pinene system goes up to 40 ppb, but only up to 10 or 15 in the o-cresol-AP system. So definitely non-negligible difference, I think this merits a direct mention.
- Line 691: very good point about the role of different oxidants. Therefore important to try to quantify the effects of each one

- Line 698: absolutely, OH yield can be very non-negligible. I believe it is close to one for  $\alpha$ -pinene ozonolysis.
- Line 701: how do you continuously inject NO<sub>3</sub>? I don't think it's available in a bottle. So you would need to generate it from O<sub>3</sub> and NO<sub>2</sub>. Of course, you can play with the ratios to minimize O<sub>3</sub>, but still
- Line 702: NO<sub>3</sub> from NO<sub>2</sub>+O<sub>3</sub>: you get this in your system as well, right? Did you try to quantify it?
- Line 706: "as much complexity as can be envisaged": this is what you're doing here
- Lines 711 - 712: True, but you might still get some mechanistic insight
- Line 722: use of a chemiluminescence O<sub>3</sub> monitor would help. Not suggesting this to be done in this study, but for broader relevance
- Line 725: yes, OH measurement would be nice, but not trivial
- Lines 756-757: A comparison of first order wall loss and condensation sink should be included. The different SOA amount could also affect partitioning: in high SOA cases, even higher volatility vapours condense, and can exaggerate the SOA difference further
- Line 760: yes, vapour pressure differences between products. But will there be differences of vapour pressure dependencies? Also, again the CS and SOA amounts are very different, so this will cause differences
- Line 768: what are Odum curves?
- Line 786-787: Even methane can have a quantifiable SOA yield in a mixture. See this Bianchi et al. paper: <https://www.sciencedirect.com/science/article/abs/pii/S1352231016304691>. As it deals with mixtures, it would probably be good to cite in any case
- Lines 788-792: see my comment about the yield calculation and exclusion of isoprene above
- Line 793: again, I think a more logical comparison would be "experimental higher than predicted"
- Line 800: this is a very good point. Small changes in e.g. the ratio of  $\alpha$ -pinene OH/O<sub>3</sub> oxidation can cause big changes in the yield. More quantification/discussion of the contributions of individual oxidants in different experiments could be useful.
- Line 810: "metastable aqueous electrolyte solution aerosol": what does this mean? Deliquesced? I feel this is being said in an unreasonably complicated way
- Line 811: "act as absorptive mass": what do you mean with this? At least in the  $\alpha$ -pinene case, you would get organic mass even without seeds, so the seed doesn't need to be very good at promoting condensation.
- Line 812: From fig. 13, how can you deduce the particles are internally mixed?
- Lines 846-848: Something like this should be mentioned already in the results. Also, can it be used to interpret the differences in this case?

- Line 852: are there real differences in the isomeric contributions? To me these seemed like they could very well be the same. And again, this whole discussion should be in the results already
- Line 860: if these are already reported in detail elsewhere, are they needed in this manuscript?
- Lines 863-864: again new results in discussion. Please move this to results, and if you want to present it, add a bit more detail
- Lines 870-871: Similar yields, different volatility distributions. This isn't necessarily conflicting, if you detect, in absolute numbers, more of the stuff that has higher volatility. Also if you are blind to some low volatility components. But the point of additional investigation is good.
- Line 872: "three example systems, chosen for...": this should have been said already in the results
- Line 876: "change in rate of formation": I'm not sure if the rate plays any role, just the formation in general
- Line 902-903: are the filter results so essential as to dictate the concentration regime?
- Lines 930-931: I don't think this is the case
- Line 940: "will depend on the rates": I don't think it's evident that it would be rate dependent

#### A list of technical comments

- Lines 48-50: long and hard to follow sentence. Now it reads as "primary pollutants are easy to understand, but secondary pollutants make substantial contribution". Maybe break sentence in two?
- Line 51: isolated --> individual
- Lines 58-60: hard to follow sentence, break up. Also, add references
- Lines 106-107: Rephrase sentence, now meaning unclear
- Lines 108-110: Long sentence, hard to follow. Also, does this sentence refer to only mixtures? As already Ehn et al., 2014, have made some attempt at quantifying the HOM fraction of SOA
- Lines 144 - 146: long sentence, hard to follow
- 167-168: Example of a sentence that would probably be best broken in two
- Lines 172 - 173: "comparable rate of change of oxidation products into the mix": this is expressed in a hard to follow manner. Do you mean "similar oxidation rates"?
- Line 185-186: meaning of sentence unclear

- Line 187: "manmade VOCs" this sounds to me like "synthetic VOCs", and they are not necessarily synthetic. I would change to anthropogenic
- Line 191: "This straightforwardly..." what is "This"?
- Line 192: "injection of liquid organic components" I understand what you mean here, but it sounds a bit funny here as you just said they are in the gas phase. At least change to "vapourised liquid..." or similar
- Line 192-193: This whole sentence is again very long and hard to follow. What exactly enables the comparability?
- Line 193-194: yes, future work could use solid precursors. However, I don't think it would be straightforward ("readily"). Also, does it merit mention in this manuscript?
- Line 204: "entrainment": wouldn't mixing be more understandable?
- Line 232: "physical space": what does this refer to? Temperature? You could try to help the reader a bit more, now it is at times tedious to read the text
- Lines 237-238: the title of this subsection is "a, b and c objectives". Now you say that the objectives were outlined in section 1: then what is the point of this subsection?
- Lines 258-260: hard to follow sentence. Also, how do the full, half and one third reactivity single precursor systems contribute to mapping the binary and ternary systems? Also, only a-pinene had all of the 1, 1/2 and 1/3 experiments
- Line 633/Fig. 11: dot area or diameter is sized?
- Line 679: maybe open the PSS abbreviation again?
- Line 681: replace +ve with positive
- Line 699: open TME abbreviation
- Line 699: "access OH decay": what does this mean?
- Line 700: does the source VOC refer to TME here?
- Line 705: "access OH consumption of saturated compounds": what does this mean?
- Lines 852, 861: add "in preparation". Also in other instances
- Line 856: "present changes": changes are not presented, instead O:C ratios are
- Line 897: sounds like you are contrasting lab studies to chamber experiments
- Line 908: infinite?