

The reviews of our paper are thorough and well-considered. We would like to thank the referees for their obvious effort in reading, understanding and critically reviewing our manuscript and for the improvements that they have helped us make.

All referees requested some simplification, clarification and shortening of the manuscript to some extent and we have taken this on board in the revision, with restructuring, shortening and modification in the focus.

We'd like to thank Referee 1 for their positive comments and to respond to the general and detailed clarifications, criticisms and suggestions as follows (reviewer comments in italics, line and Figure numbers refer to the original discussion manuscript for clarity):

*All in all, the manuscript details a large body of work and analysis, and for this the authors are to be commended.*

Thanks for this; it's appreciated.

*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.*

The referee recognises the challenges associated with the presentation of the breadth and scope of material. Clearly our original manuscript did not succeed in optimally delivering the messages we aimed to convey.

*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.*

We have taken this on board in the revised manuscript and tried to ensure a more logical and informative ordering and prioritisation of material.

*- 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*

Much of the difficulty arises here because of the attempt to squeeze too much detail into the current paper. We have addressed this largely by referring to our subsequently published manuscripts where more detail has been presented and by moving of much of the material (including results) from the main

text to the supplementary. We have, however, retained necessary information in the discussion, referring to the supplementary material and other publications, where necessary.

*- 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.*

Again, the sequencing of the writing and publication of our work has led to challenges that are more readily resolved now that more of the material has been published. We have cited this work earlier in the revised manuscript.

*- 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.*

As mentioned above, we have moved all the figures related to other papers in the SI and bring them forward only for the discussion.

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

All captions have been updated to provide more information as required.

*- 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.*

All core data (covering everything from Figures 1 to 6) from all experiments will be provided through the open access EUROCHAMP database. A link and doi will be provided with the final paper. There are some challenges with data formatting for the more complex and large mass spectral data but as much data as practical will be uploaded to the database from all instruments, with the full data available on request.

*- 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.*

We have now tried to use plain English wherever possible. Some of the concepts are complex and challenging, but we have attempted to clarify as much as we can.

*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.*

First order wall loss rates of non-volatile vapours have not been experimentally determined as a function on their vapour pressure as would be necessary to fully evaluate this. Indeed, it is an area of heated scientific debate. Such a treatment is explicitly included in the PyCHAM model presented in O'Meara et al., (2021; <https://doi.org/10.5194/gmd-14-675-2021>) with a sensitivity to the tuning parameters in Figure 7. It is unclear that any reasonable amount of seed will present sufficient mass to be the main sink for all volatility classes, depending on the efficiency of the uptake. A discussion of the implications of these effects is now included in the revised manuscript, but care is made for it not to become the main focus of the paper,

*- 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  $(100*0.1 + 100*0)/200 = 0.05$ . Excluding isoprene it would just be 0.1. Predicted mass, in the first case, would be  $0.05*200 = 10$ , while in the second case (again excluding isoprene) it would be  $0.1*100 = 10$ . 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?*

Our discussion of the inclusion of isoprene in the yield calculation relates to whether a low yield precursor should be included in the reference case for the yield. We agree with the reviewer that there is no difference in predicted mass when including or excluding isoprene, but the predicted yield is different owing to the denominator in the yield calculation being the consumption of the VOC – should the yield in a mixture include all VOCs in the mixture, or just those that might turn out to be precursors. It is not a purely academic argument and we discuss the predicted yield difference in both scenarios (and the implications on whether the yield is suppressed, enhanced or unaffected).

*- 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.*

This is rephrased accordingly.

Figure 5 has been updated for clarity.

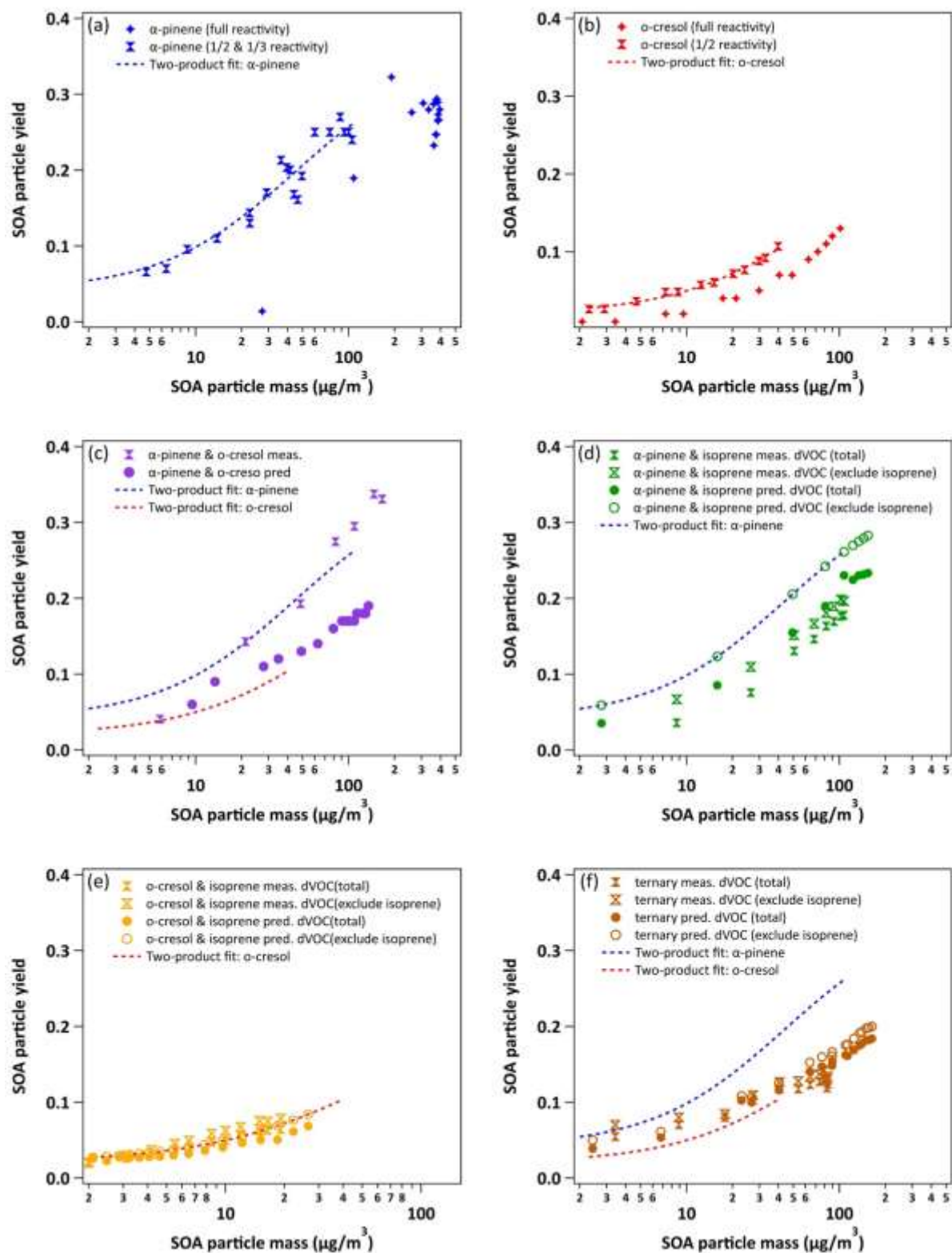


Figure 5. Yield data for selected representative experiments in all systems (with two-product yield curves for  $\alpha$ -pinene and *o*-cresol single VOC experiments). Panel a) shows the measured/predicted yield versus SOA mass in the single VOC  $\alpha$ -pinene system, Panel b) single VOC *o*-cresol system, Panel c) the binary  $\alpha$ -

pinene / *o*-cresol mixture, d) the binary  $\alpha$ -pinene / isoprene mixture, e) the *o*-cresol / isoprene mixture (expanded y-axis plot shown in Figure S5) and f) the ternary mixture. Yields “predicted” from the linear combination of yields from the individual VOC experiments in panel a-b using equation 4 are shown for each mixture.

- 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.

We agree with the reviewer that Table 4 should be presented graphically and additionally replace Table 3. The new Figures 5 and 7 (shown below) are included in the revised manuscript.

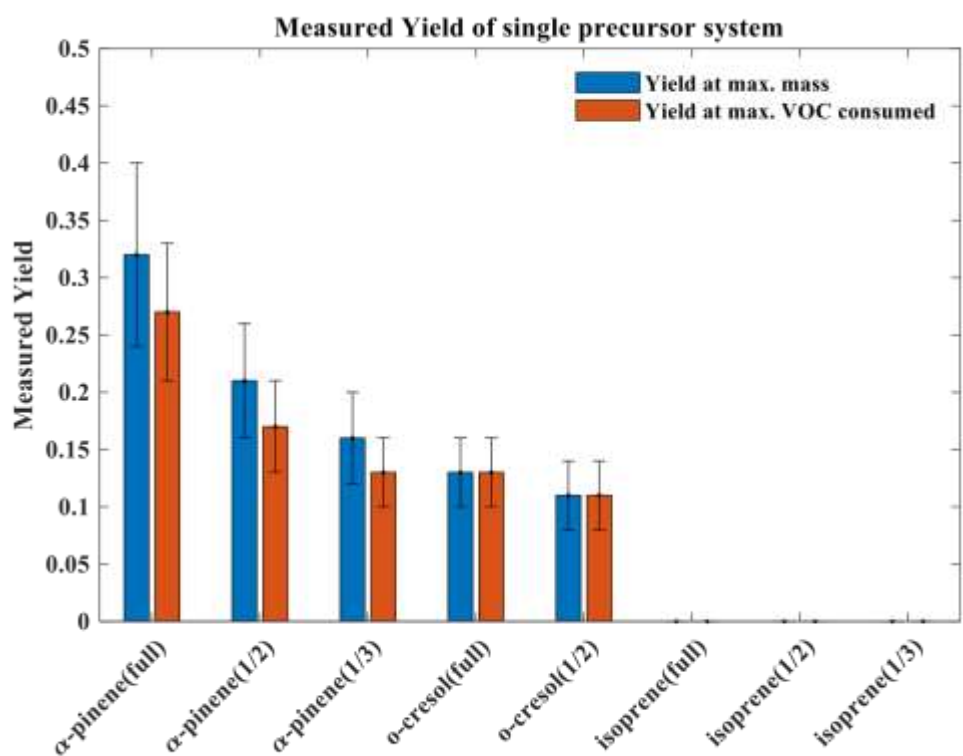


Figure 5: Measured yield for all single precursor system calculated at maximum particle mass and maximum VOC consumed

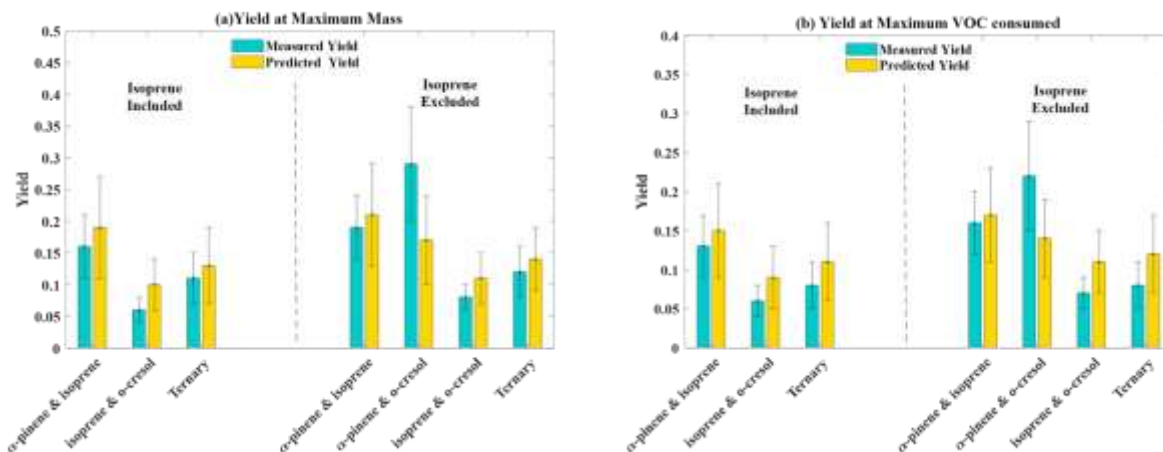


Figure 7: (a) Measured and Predicted yield for all mixture precursor system calculated at maximum particle mass; (b) Measured and Predicted yield for all mixture precursor system calculated at maximum VOC consumed. For mixtures containing isoprene, which had zero yield on the neutral seeds injected, the yields were calculated excluding the consumption of isoprene in the system allowing them to be referenced to the mixtures without isoprene. Yield was calculated with the density of organic matter of  $1.4\mu\text{g m}^{-3}$ . The maximum mass used in the yield at maximum mass calculation is given in Table 1. The uncertainties in SOA particle mass yield were calculated by propagating  $\pm 1\sigma$  uncertainties of predicted  $\Delta\text{SOA}$  and measured  $\Delta\text{VOC}$ .

- 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.

These are addressed in response to the specific comments below.

*A list of individual comments related to the content*

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

Removed repetition

- 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

Removed from abstract and defined early in the main text

- 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.

We do indeed calculate that it is the dominant oxidant in most cases, however it was not known that this would be the case at the planning stage of the experiments. We use it in the first instance and explain that this it was an assumption at the point of the planning of its use.

- line 44-45: add a very brief description of what SOA is

Added

- 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

We agree. The sentence has been rephrased

- Lines 60-61: "SOA formation is considered less mechanistically": is this so? Please add reference

We contend that this is the case, since the mechanisms of SOA formation are still highly uncertain – especially the interactions between VOCs in mixtures and the dependence of condensing products on the chemical regime. The review of Shrivestava et al. (2016; <https://doi.org/10.1002/2016RG000540>) provides a good review of the underlying assumptions in current models and requirements for further mechanistic investigation.

- Lines 76-77: add reference

Sentence deleted and added as a phrase to the sentence on lines 79-81.

- Line 79: "OH controlled by isoprene": Berndt et al also provide another (possibly more plausible) mechanism: would be good to mention it already here

Indeed, Berndt et al., (2018) highlighted the importance of the RO<sub>2</sub>-RO<sub>2</sub> accretion product formation and their potential significant contribution to the SOA particle formation and growth, showing that presence of isoprene inhibited α-pinene C<sub>19-20</sub> dimer formation and increased the C<sub>15</sub> products.

Accordingly we have amended the sentence:

"It was established that the scavenging of the OH radical by addition of isoprene significantly inhibits new particle formation in plant chamber studies (Kiendler-Scharr et al., 2009) and subsequently Berndt et al. (2018) showed that the presence of isoprene could inhibit the production of dimers that can be involved in nucleation or early particle formation."

- Line 79-81: I think Berndt et al have very similar conclusion, so would be good to cite them as well

Citation added

- Line 85: both ethylene and isoprene

Added

- Lines 97-98 Add reference

We have added the example reference to Bianchi et al. (2019)

- Line 102: doesn't the Bianchi et al HOM definition only include autoxidation?

This is indeed the case. The distinction has been made, though it is rather clumsy. The exclusion of non-oxidation-derived highly oxygenated molecules is recognised in the revised sentence.

*- Lines 154-156: Are you using these arguments or not?*

We are simply choosing daytime oxidants without making any argument about the relative importance and using this as a starting point for studies using our approach. We would encourage a similar approach using isoreactivity towards dark oxidants, though such experiments will have their own challenges related to in-situ vs continuously injected oxidant, for example.

*- 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*

We agree. Sesquiterpenes have been used as an illustration only and "in particular" was poor phrasing. An, admittedly rather old, reference with a table of atmospheric lifetimes is provided by Atkinson and Arey (2003)

*- Line 171-172: you just said that reactivities vary, so similar concentrations are more of an exception than a rule, right?*

Indeed, but so are mixtures of only 3 precursors. The many thousands of ambient VOCs will include many of comparable reactivity and many of highly variable reactivity in the same air masses. We do not claim that such a simple system is atmospherically-representative, but that our framework and choice will allow evaluation of interactions where no single precursor will dominate the oxidation products. It is necessary to start studies of mixtures somewhere and we are proposing one particular approach in the absence of others.

*- 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.*

In the context we have used it, we agree with the referee and have changed it.

*- 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*

We have been less obtuse in the revised manuscript

*- 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*

OK. We have replaced the offending phrase

*- Line 199: "earlier formation of SOA mass": I would rather say higher, as it enables larger fraction of condensable compounds to go to particles, as opposed to walls. Esp. in batch mode this also translated to higher overall mass*



The higher mass results because of the earlier formation of significant mass, enabling the partitioning of vapours formed in the early stages of the experiment to the particles rather than to the walls, which would occur preferentially in the absence of seeds whilst waiting for the onset of nucleation. We have revised the sentence in the manuscript to state "...earlier and hence greater SOA particle 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  $\alpha$ -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.*

The morphology of particles is unknown – all seeds were nebulised from stock solutions and likely maintained as metastable aqueous particles at the chamber RH and the concept of "coating" is questionable. Nevertheless, the mass fraction of SOA in the particles will indeed vary and the partitioning through uptake to the strong aqueous solutions and subsequent dissolution / absorption may well vary between systems. This is recognised in the revised manuscript – though again we stress that it is not a primary focus of the paper.

*- Line 206-207: this implicit assumption may not hold, see previous comment*

Whilst it may not hold because of the complexities recognised in our reply above, as shown in Fig. 5, we plot yield-SOA mass curve, and compare the yield in different systems at the same SOA mass (absorptive mass). Comparable inorganic seed provide similar condensation medium at the starting point.

*- Lines 204-207: again a very long sentence, better break in pieces.*

This argument is now made in smaller bite-sized chunks.

*- 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*

There have never been any experiments in the chamber with addition of NH<sub>3</sub> above the ambient concentrations and all brand-new bags exhibit the same behaviour. We do not believe our chamber behaves substantially differently to other Teflon chambers and are unaware of others of being able to hold reasonably low concentrations of acidic seed for extended periods. There may be further implications, though they have not been systematically explored.

*- Seed generation in general: are the seed particles dried or not? So are they effloresced or deliquesced?*

Seed particles are generated by atomizer and injected into chamber without drying. So after the atomizer, the seed is deliquesced prior to injection into the chamber held at ~50% RH, such that the particles are likely metastable aqueous solutions at a water activity of around 0.5.

*- Line 209: supposedly also potential saturation at high signals? And what do you refer to with the "sampling requirements"?*

At the concentrations we are working with the detection limit is more of a problem than saturation. Should we have wished to work at higher concentrations, saturation would be more of a problem.

Sampling requirements include the need to obtain sufficient mass on the filters for offline analysis at the end of the experiment above the chamber background concentrations, for example.

*- 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)*

In our case, the detection limits for these instruments are low and this is added to the sentence.

*- Line 220: the fact that the chamber is teflon should be mentioned already earlier*

Now added to line 123

*- Line 221: so are they a challenge or not? "modest challenge" sounds like yes, but "unnoticeable" sounds like no*

They could be a modest challenge if the VOC:NOx ratio requirement was more rigorous (i.e. we wanted to work at a specific low VOC:NOx ratio which may have been above a couple of ppb). Since our choice was to work at the VOC levels stated, there was no noticeable problem. Our wording in this sentence was precise and not contradictory; we have qualified "modest" by adding "at worst".

*- Line 223: "simulated solar spectrum" do you have a reference for this?*

This is in Shao et al. (2022a), citation added.

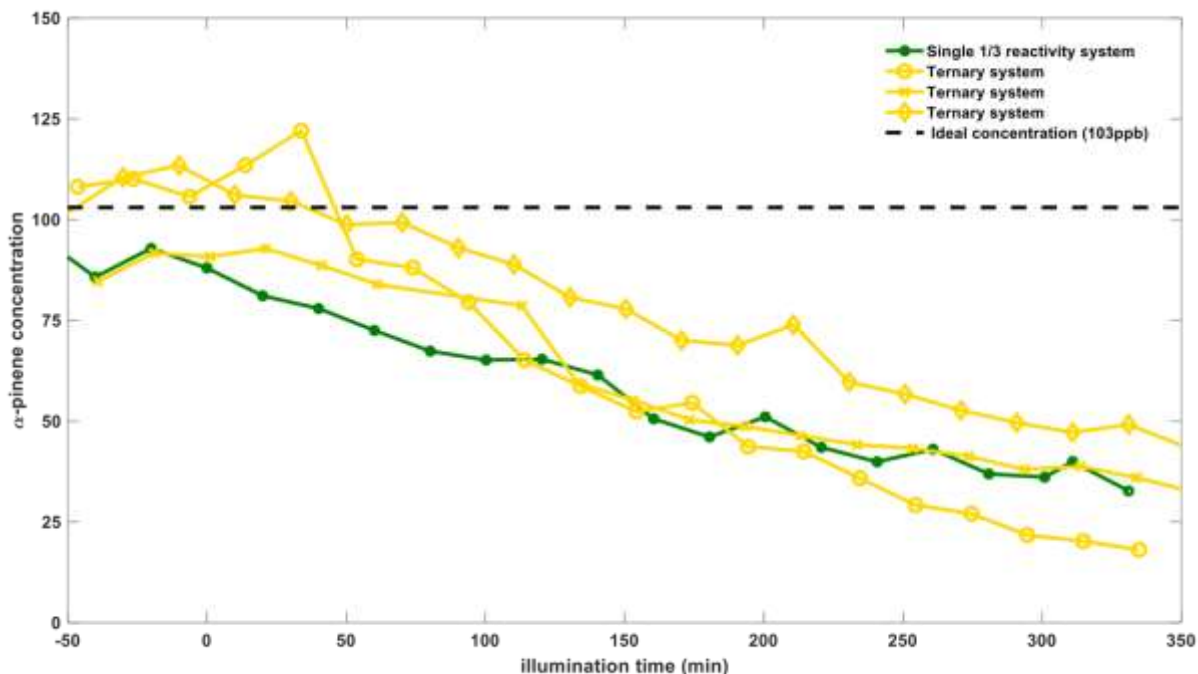
*- Line 225: do you have a quantification of the vapour wall loss? Can you present a comparison to condensation sink? What is "sufficiently large"?*

See our answer above. Now we do not have a definitive quantification of the vapour wall loss, which is not the primary focus of the manuscript, though we recognise its importance. No such direct "comparison with the condensation sink" is possible, since the walls and particles are not equally available to the molecules in the chamber (the particles being well-mixed and dispersed across the volume, and the walls being within a few mean free paths of only those molecules very close to the walls and able to traverse the boundary layer existing in the chamber under our mixing conditions). As mentioned, this is subject to heated debate and is not the focus of the current paper. We injected seed sufficient to suppress observable particle formation. Without seeds, nucleation and growth occurs in all  $\alpha$ -pinene containing systems and the *o*-cresol system at our concentrations. This is an experimental demonstration that the seed concentrations we use competes effectively with the walls for the vapours.

*- 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*

Initial VOC concentrations are based on the volumes of the initial injected precursor and an assumed efficiency of injection and evaporation into the chamber. This has been verified in several  $\alpha$ -pinene experiments from direct measurements calibrated using standards (see below figure). The same efficiency is assumed for all VOCs and initial concentrations were then calculated, applying a  $\pm 15\%$  nominal

uncertainty to account for injection variability. The measured signal decays were then used to evaluate the VOC decay trends.



Standard calibration of initial  $\alpha$ -pinene precursor for the GC-MS measurement in different systems

- Lines 250-251: most of the work is on different single and binary systems, but here you only mention the single ternary system

We recognise that this was ambiguously stated. When referring to the ternary system here we were referring to the entire programme of experiments rather than the ternary experiment. Changed to “3 VOC”.

- Line 256: what does isoreactivity mean? Is this a concept defined by you? If yes, you should make it very clear

Clarified in the revised script. It's not a difficult concept, just a useful tool that we have devised.

- Line 257: so is this purely calculated ratio, not measured? But it is presented as a measurement result in table 1?

The ratio is indeed calculated and not measured. The volumes corresponding to these mixing ratios were injected with a nominal “injection uncertainty”, with verification for several calibrated  $\alpha$ -pinene measurements to within this uncertainty (see Figure above). We have expanded the footnote in table 1.

- Lines 260-261: values for which precursor? Also, give reference

Initial full-reactivity mixing ratio in the 100s ppbv for  $\alpha$ -pinene and o-cresol precursors respectively, were expected to provide 10 to a few 100  $\mu\text{g m}^{-3}$  SOA particle mass yields (Henry et al., 2008; Nakao et al., 2011; Eddingsaas et al., 2012).

- Line 266: *what are the others? Again, help the reader a bit more. What about nitrate radical?*

Nitrate radical oxidation will be negligible under the chosen photo-oxidation conditions. We already mentioned ozone in the sentence, but have made it explicit that ozone is the other one.

- 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?*

We have moved the methodology section 3 into a subsection of section 2 whilst still attempting to ensure the design of the experiment is understood before being stated.

- 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*

NO+HO<sub>2</sub> produces OH, so not a net loss of HO<sub>x</sub> – it is a well-known coupling between the HO<sub>x</sub> and NO<sub>x</sub> cycles in standard VOC degradation in the presence of NO<sub>x</sub>. A reference to a standard text is made in the repositioned methodology section.

- 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?*

Yes; decay rates were probed by both direct measurement (see figure 2) and, within measurement limitations, calculation of oxidant contributions (see figure 6). Without modelling the systems, it is not possible to evaluate the magnitude of the coupling between the change in ozone production and the VOC decay rate, though the ozone measurements can be used to estimate the relative contributions of the oxidants.

- Line 276 *How is the ambient OH reactivity relevant here? And its measurement methods?*

It demonstrates that our concentrations lead to a comparable oxidant turnover regime to the ambient atmosphere. The closure between ambient VOC abundance and direct measurement of OH lifetime gives confidence that the former (which we use in the chamber) is a reasonable predictor of the latter.

- Line 278: *did you measure this?*

See last reply. OH reactivity was calculated based on the initial concentration and the reaction rate coefficients, not measured. However, we have confidence that these are reasonably calculated referring to the ambient closure.

- Lines 279-280: *why would it be desirable? For atmospheric relevance? Then explicitly mention this*

We have now explicitly mentioned that a comparable turnover of oxidant can be achieved at atmospherically reasonable oxidant concentrations at our VOC concentration.

- Lines 284-285: Give reference

Example reference given: Yang et al., (2016)

- Lines 285-286: Good point, a common feature in chambers. Reference?

It is not widely and thoroughly characterised in all chambers, but a good relevant study of the situation in oxidation flow reactors is: Peng and Jimenez (2020)

- Line 303: inlet to the chamber?

Clarified – it is the inlet air system for the chamber

- Line 311: as gaseous contaminants, I would be more concerned of organics than NO<sub>x</sub> and O<sub>3</sub>

A description of the MAC infrastructure, characterisation and operating procedures can be found in Shao et al. (2022a). We incorporate an activated charcoal scrubber for VOC in the inlet system. We do not routinely measure VOC in the pre-experimental procedure, but regularly monitor the VOC and oxidised VOC background in the bag using GC-MS and CIMS. When contamination is unacceptably high, e.g. such that it leads to a particle mass background on harsh oxidation of greater than around 0.5 µgm<sup>-3</sup>, we undertake to change the bag.

- Lines 321-322: particles are not size selected? Maybe mention this

We inject a polydisperse particle population. This is now stated.

- Line 357: actinometry and off-gassing experiments: please give more details

Off-gassing is clean air+light (or background experiment). Actinometry clean air + injected NO<sub>2</sub> + light and both are described in Shao et al. (2022a)

- Lines 362-364: this should be mentioned way before

This is now subsumed in the repositioned methodology section

- Lines 376-378: this should be mentioned in the caption as well

The description was added into the caption as suggested, which reads as '**Figure 1:** NO<sub>2</sub>, NO and O<sub>3</sub> time series in example single and mixed VOC experiments (a) α-pinene, (b) isoprene, (c) α-pinene/isoprene, (d) o-cresol. Note that, in the presence of o-cresol, O<sub>3</sub> measurement by UV absorption was influenced by UV absorption by o-cresol and O<sub>3</sub> data in (d) were corrected as explained in the methods section.'

- 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.

NO background in our chamber is limited to a few ppb, owing to our inability to scrub the NO<sub>x</sub> from the laboratory levels at ambient concentrations at our high inlet flow rates, despite passing through our Purafil filter. We never aim to conduct NO<sub>x</sub>-free experiments and work with a few ppbv NO background. NO, NO<sub>2</sub> and O<sub>3</sub> initially move towards the photostationary state, with O<sub>3</sub> being produced from NO<sub>2</sub> photolysis. The VOC oxidation then leads to additional ozone production as VOCs are consumed through the NO reaction with HO<sub>2</sub>. The system then attempts to attain the continually evolving photostationary state. OH is formed through the photolysis of O<sub>3</sub>. In the case of an unsaturated biogenic VOC, there is O<sub>3</sub> consumption through reaction with the double bond and secondary OH formation. Cresol only undergoes oxidation through OH attack, not ozonolysis. The complexity of the photochemical system means that it is not straightforward to predict initial trajectory of the NO<sub>x</sub> and O<sub>3</sub>.

- Fig 1.: *In the a-pinene/isoprene case, why is the NO so low compared to either single case?*

We have not fully chemically modelled each system. Whilst the background NO is non-negligible and variable, the VOC:NO<sub>x</sub> is initiated at comparable levels in each experiment, including the background. Our dataset is extremely rich and the evolution of chemistry in these systems should be a study in itself, combined with our developing PyCHAM modelling capability.

- Lines 407&413/ Fig. 2: *is standard deviation a relevant number for such a small number of experiments?*

We now show the “envelope” of the measurements across the experiments to demonstrate the variability. We agree that standard deviation should not be used for such low numbers and Poisson statistics would be more appropriate if we were to make a rigorous statistical analysis

- Lines 416-417: *add reference*

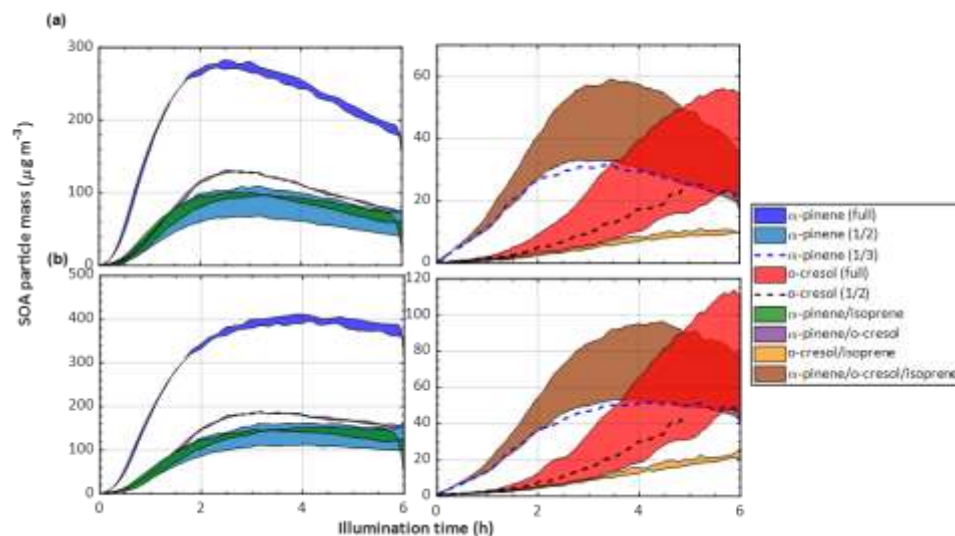
Reference added: Henry et al., (2008)

- 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"*

Rephrased: “The incomplete VOC consumption in the experiments can be seen in Figure 2’

- Line 421/ Fig. 3: *particle mass peaking in o-cresol experiments is hard to see in the plot. Maybe separate into subplots?*

The Figure has been plotted as 4 sub-plots as shown below



- Line 433. This paragraph discusses a figure in the suppl. Could the whole paragraph be moved to the suppl?

As with other supplementary Figures, the results are no longer presented in the main text, though are included in the discussion.

- 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

Each curve comprises multiple measurement points over the duration of each experiment. This has been clarified in the revised caption that reads:

“Figure 4: SOA particle mass yield as a function of mass formed in the single precursor  $\alpha$ -pinene and o-cresol experiments at all initial concentrations. Each curve is comprised by multiple data points measured over the duration of each experiment. Error bars represent the propagated uncertainties in all measurements and in the particle wall loss corrections applied.”

- Line 491: *hypothetical particle mass*

“hypothetical” now added

- Line 496/505: *I think this is the most important figure of the paper, but it is pretty hard to read*

Updated, see figure in the response above

- Line 504-505: **How is this "indeed"?**

“Indeed” is removed – we agree that the argument is too convoluted and complex to expand.

- Lines 507-509: *see my comments about including isoprene in the yield calculations above*

See our responses to these comments. It is not a trivial point and the reference point for yields in mixtures is an important consideration.

- 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*

See our response above, new figures 5 and 7 replace tables 3 and 4.

- Lines 546-547: *please compare both the same way, i.e. ozone compared to OH for both, or then vice versa*

This has been reworded

- Line 554/Fig. 7: *Expand caption, now this tells very little. This is a common problem with other captions as well*

This figure is now in the SI with an expanded caption: **Figure 7.** Time series of the signal fraction of  $m/z=44$  (panel a) and  $m/z=43$  (panel b) in total organic signal measured by AMS, representing more and less oxygenated contribution to total SOA mass.

- Line 567: *"the reverse is true": what is the implication?*

This can only be speculated at this point and warrants further exploration. Again, Figures 7 to 13 have been moved to the SI since the results are much more extensively explored in our companion papers, along with the remaining open questions.

- Line 570-571: *Makes sense. Though they are pretty different chemically also otherwise, not only in carbon number.*

A note to this effect is made in the revised sentence.

- Line 587/Fig.8: *Again, more info in caption. Like that this is particle phase*

This figure is now in the SI, the updated caption reads as follows: 'Figure S8: FIGAERO-CIMS particle-phase Mass spectra taken in the single precursor  $\alpha$ -pinene (a1 and a2), *o*-cresol (b1 and b2) and mixed  $\alpha$ -pinene / *o*-cresol system (c1 and c2) at 0.5 hour (a1, b1 and c1) and 5.5 hours (a2,b2 and c2) after the onset of photochemistry in the MAC. These mass spectra have been normalised to the same reagent ion ( $I^-$ ) concentration. There is a clear increasing signal in the  $m/z$  range from 200 to 600 ( $I^-$  adducts) after 5.5-hour reactions in single and mixture systems corresponding to the increase in detected particulate products with the increase in SOA particle mass with time. It indicates the changes in particulate mass spectra of single  $\alpha$ -pinene and *o*-cresol experiments and their mixture via the measurement from FIGAERO-I-CIMS instrument. Additionally, some unique peaks (e.g.,  $m/z$  358, 403, 419, 439, etc) are only detected in the mixture mass spectra. Peak assignment of these mass spectra has been used to attribute signal to the molecular formulae and hence to broad chemical groupings in all single VOC and mixed systems. A full analysis and discussion can be found in Du et al., 2021 (in prep).'



- Lines 594-595: Why does the negative mode show predominantly *o*-cresol derived products, but positive *α*-pinene derived?

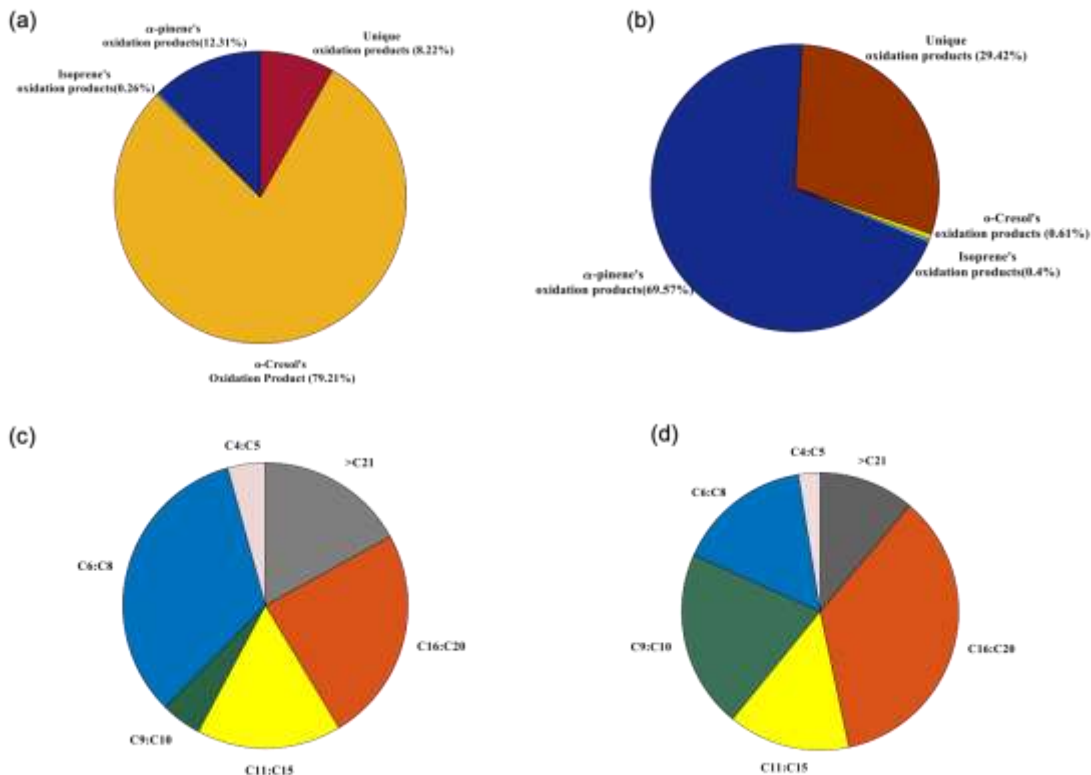
The CHON compounds, dominated by nitro-aromatics in *o*-cresol photo-oxidation were found to make significant contributions in the ternary system owing to the high sensitivity in the employed electrospray ionization method. More detailed discussion of the molecular composition in each system obtained from LC-Orbitrap-MS is discussed in Shao., et al (2022b) along with the reasons for the relative contributions.

- Line 595: was retention time used in the identification as well?

Yes, the retention time was used in the identification for the offline LC-MS analysis. The detailed information about the LC-MS data analysis can be found in Pereira et al., (2021), Du et al., (2022) and Shao et al., (2022b).

- Line 596/Fig 9: change the panel order to a-->b-->c-->d

Figure 9 had been revised as shown below and moved to Supplementary material as Fig.S9. The sentence in line 596 has now been rephrased: "This is shown for molecules detected in negative , panel a), and positive ionisation mode, b). The LC-Orbitrap-MS detected components uniquely (Unique-to-mixture) found in the ternary system have been split by contribution to the signal by carbon number in panels c) and d) for negative ion and positive ion mode respectively."



- Line 599, also elsewhere: spell out -ve and +ve

The -ve and +ve have been changed to negative mode and positive mode, respectively throughout.

- 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

All the labels have been changed to "Precursor's oxidation products" in Figure 9 as shown above.

- Lines 609-610: the sentence is hard to follow.

Changed to ' LC-Orbitrap-MS is able to separate isomers. One example from the compound  $C_7H_7NO_4$  (methyl-nitrocatechol and its isomers) in *o*-cresol containing systems is shown in Panel a) in Figure 10.'

- Lines 612-613: Are there any real differences between experiments?

Whilst there are few differences in the isomeric contributions across systems, panel a) should be viewed in conjunction with panel b), with b) showing that the temporal behaviour of the sum formula component is different. Whether there is a different fractional contribution of isomers with time in the various systems is not known and should be a focus of further work.

- Line 614: mention that this is particle phase

Mentioned

- Line 618/Fig. 10: what is the normalized peak are? 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?

The normalised peak area is that the peak area of each compound is normalised to the total peak area of all detected compounds. It is the fraction of a compound to the total signal.

The normalized peak areas are calculated in the same way for the LC-MS and FIGAERO-CIMS . The results vary between the two instruments because compounds detected by the two instruments, the peak area of each compound and the total peak area from each instrument are different. LC-MS can separate isomers of compounds and FIGAERO-CIMS cannot. More information about the comparison in the characteristics of chemical composition between the two instruments was provided in Du et.al. (2022). The raw data are available. The results from the last FIGAERO desorption which happened after 5.5 hours of experiments and the samples for LC-MS analysis were collected at the end of experiments (after ~6 hour of experiments). The chemical composition almost reached steady after 4.5-hour reactions from the FIGAERO results, as shown in Du et.al. (2022) and Du et.al (in preparation). Therefore, the results from the last FIGAERO desorption can be employed to compare with the results from the LC-MS. However, the purpose of Figure 10 is to demonstrate the capability of offline LC-MS and FIGAERO-CIMS, which are able to separate isomers of a compound and provide time-series behaviour of a compound, respectively.

The increasing trends in the o-cresol trace is plausibly consistent with the increased SOA mass formation in single o-cresol systems after 3-hours reactions (Fig 3). However, no specific experiments were carried out to show the relationship between the SOA mass and the trace mass. More work is needed to identify the reasons behind this phenomenon in future.

- Line 625: *change showing to implying etc.*

Changed.

- 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*

According to Voliotis et al., 2021, either of the two volatility estimation techniques is able to illustrate the volatility changes between systems. The purpose of this section is to highlight the changes in the properties of the SOA particles due to the mixing of the precursors rather than to get into details about the different techniques employed. Therefore, the selection of the FIGAERO-CIMS results instead of the TD-AMS was just incidental, similar points could have been made showing either. A full discussion about the characteristics of each technique and their implications can be found on the related paper (see Voliotis et al., 2021a).

As can be also found in Voliotis et al. 2021, the volatility distributions from the FIGAERO-CIMS have been calculated based on the gas to particle ratio of the identified species. In more detail, the FIGAERO-CIMS signals in both gas and particle phases were converted into concentrations ( $\text{ions m}^{-3}$ ) based on the signal strength and the volume of air sampled. Using the fraction of each species in the particle phase (i.e., partitioning coefficient) and the total absorptive mass (in this case the total organics concentration), the saturation concentration of each identified product was calculated (see Donahue et al., 2006).

This description along with the figure are now in the SI rather than the main text of the paper.

- 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*

We have now moved everything from Figures 7 to 13 from the results section to the SI, referring to them and the companion papers in the Discussion section. A brief description of the techniques employed has been added to the Methodology that is now in section 2.

- Line 641: *these cannot be found, at least not yet*

True. Voliotis et al., 2022 was still in the late stages of preparation and had not been submitted at the time. The paper now is under review in ACP (10.5194/acp-2022-312) and has been added in the revised manuscript.

- 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*

The finger is unintentional. Indeed, as discussed in detail in Voliotis et al., 2021 and Du et al., 2021 (and earlier in Stark et al., 2017), the quantification of the effective saturation concentration from the FIGAERO-CIMS is challenging for compounds with high or low  $C^*$  due to signal to noise limitations of the technique for either the particles or gases respectively. Therefore, the volatility distributions shown can be skewed and dominated by semi-volatile organic compounds.

The following text has been added in the caption of the Fig. 12 (now in SI):

“As has been described in more detail elsewhere (see Stark et al., 2017, Voliotis et al., 2021 and Du et al., 2022), the quantification of the effective saturation concentration from the FIGAERO-CIMS is challenging for compounds with high or low  $C^*$  due to signal to noise limitations of the technique. Therefore, this results in a narrowing of the retrieved volatility distributions. Nonetheless, Voliotis et al., (2021) showed that the technique can reasonably capture the volatility changes between the different systems. Here, it can be seen that the volatility distributions of particles in the mixture experiments can be similar ( $\alpha$ -pinene / isoprene) or quite different (*o*-cresol/isoprene) to those in the experiments using a single precursor. These observations suggest that the effect of mixing precursors can have a varying effect on the resultant particle volatility. Detailed discussion about the volatility changes and their predictions can be found in Voliotis et al., (2021, 2022).”

- Line 648: *what does "differences in evolution of the SOA particle components" mean?*

The change of chemical composition of the particles.

- Line 649: *you talk about all systems, but only show three. Why?*

All systems showed the same trend. For clarity, only three systems are shown as examples.

The sentence has been rephrased to make it clearer:

“Since the particles are grown on inorganic seeds, the physical properties in all systems are initially dominated by the inorganic components (Wang et al., 2021, 2022). For clarity, three example systems (*o*-cresol / isoprene, *o*-cresol and  $\alpha$ -pinene), representing low, moderate and high SOA formation rate, are shown in Figure 13.”

- Line 651: *rearrange these to match the figure. Also, what is presented is kappa, not hygroscopic growth factor?*

The sentence has been updated to: “This shows the relationship between the multicomponent particle composition, the hygroscopicity parameter (under subsaturated and supersaturated conditions from HTDMA and CCN, respectively) and the rebound fraction of particles (indicative of their phase state) as the SOA to inorganic mass fraction of the particles develops”

Indeed, we made a mistake in the text. Kappa is used in the Figure.

- Line 651: *"indicative of their phase state": give more details. Not evident for the general reader*

A sentence has been added to clarify the phase state: "Here, aerosol particles tend to be liquid at BF below 0.2, non-liquid above 0.8 and in a transition phase between 0.2 and 0.8."

- 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*

Yes, we were imprecise. The sentence has been rephrased to: "It is clear that the organic to inorganic ratio, controlled by the amount of SOA formation, determines the physical behaviour of the particles."

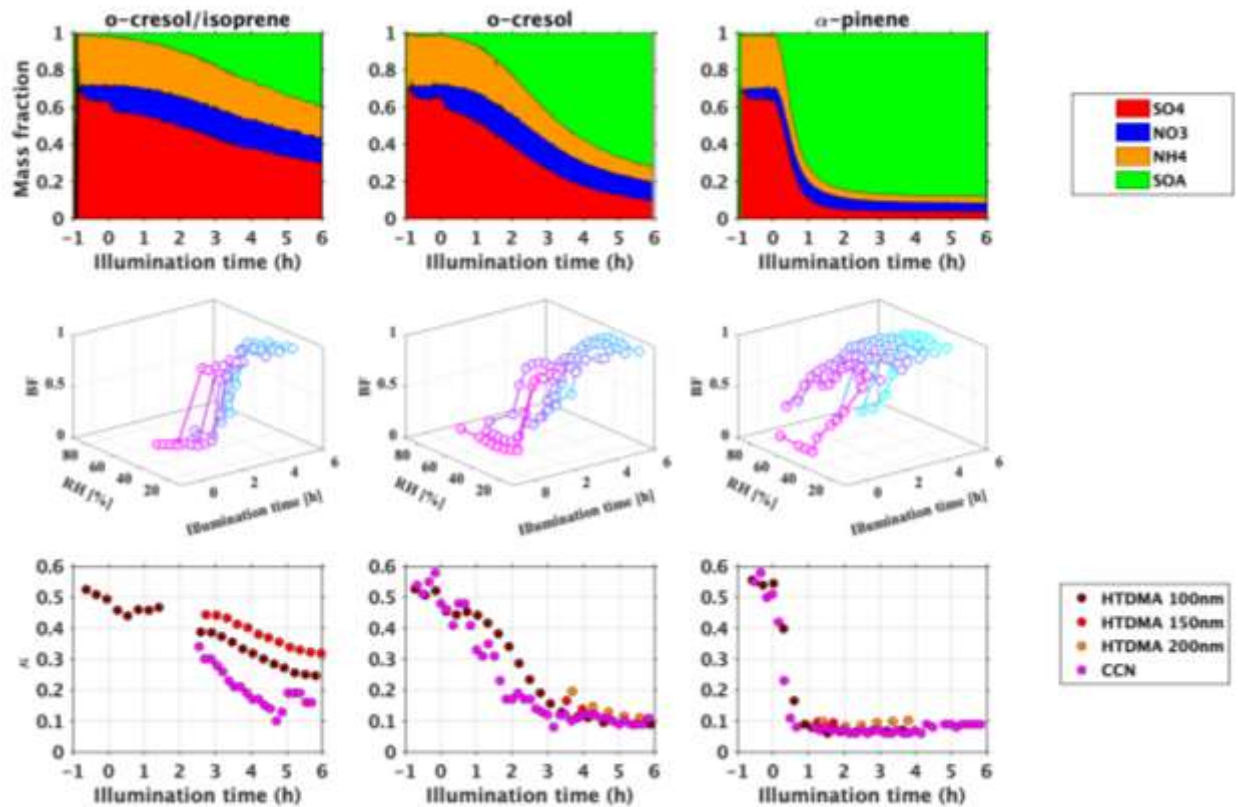
- Line 659/Fig. 13. *The figure does not show any rates, but mass fractions. Similar confusion happens also in other points of the manuscript*

The caption has been revised: "Figure 13: top row: the time series of AMS chemical composition in three example systems. The SOA mass fraction change increases fastest in  $\alpha$ -pinene systems and lowest in o-cresol/isoprene system;"

- 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?*

"increasingly rapid transition" means with respect to time in a single experiment. The sentence and figure have been updated accordingly: "middle row: the corresponding time series of Bounce Fraction (BF) at different RH between 20-85%. The transition RH from non-liquid (BF>0.8) to liquid phase (RH<0.2) increase during SOA formation evolution;"

The RH-BF subplot has been revised as suggested.



- 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.

During the experiment, the aerosol particles grow in size so that the measured sizes in HTDMA increases from 75/100nm to 200-300nm depending on the mean diameter of the number size distribution. In the o-cresol/isoprene experiment, the mean diameter of number size distribution grows less than 200nm, so only 100 and 150nm are measured in HTDMA. The kappa comparison of HTDMA and CCN is used for closure study.

Updated caption: "bottom row: the corresponding time series of hygroscopicity parameter (kappa) from subsaturated (HTDMA, measured sizes increased with time due to SOA formation) and supersaturated conditions (CCN)"

- Line 671: not only "can lead", but "does lead"

Changed to "leads to"

- Line 678: more ozone production, or higher ozone concentration?

We were imprecise and agree we cannot state that it is more production, just higher concentration. Changed.

- Line 682: what is the meaning of the low phi values?

Values of Leighton ratio below 1 could arise from a wall source of NO. Alternatively, errors propagated from the determination of  $j_{\text{NO}_2}$  from actinometry experiments and measurements of NO, NO<sub>2</sub> and O<sub>3</sub>, as well as the heterogeneity of the  $j_{\text{NO}_2}$  owing to variation in light intensity across the chamber (not reflected in the point measurements of the gases) could lead to significant errors in Leighton ratio. This but must be the subject of further work. The implications would be that the absolute values of Leighton ratio may carry unknown errors, but their trends and relative values between experiments, should be reliable. This is discussed in the revised manuscript.

- Line 683: Throughout, the term turnover is used. Maybe use oxidation rate instead? I find turnover slightly confusing in this context

Agree. We have simply referred to “decay rate” in the revised section to avoid confusion. In the absence of a production or influx of VOC, the turnover is simply the net result of the loss of parent VOC to the available oxidants which is its decay rate.

- Lines 688-689: If we trust the numbers, O<sub>3</sub> 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.

This was already directly discussed in Section 5.1

- Line 691: very good point about the role of different oxidants. Therefore important to try to quantify the effects of each one

Indeed, and this is what we have tried to do as shown in Figure 6 where the data allows. Also see our response to your comment on consumption by NO<sub>3</sub> below.

- Line 698: absolutely, OH yield can be very non-negligible. I believe it is close to one for a-pinene ozonolysis.

We absolutely agree that secondary OH formation will be important and so dark oxidation would not avoid the need to consider OH.

- 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

Continuous NO<sub>3</sub> injection is performed by preparation of frozen pure N<sub>2</sub>O<sub>5</sub> and flowing N<sub>2</sub> across the headspace. We aborted a project using this technique on these mixtures at the beginning of Covid lockdown. Watch this space.

- 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?

Indeed, the production rate of NO<sub>3</sub> can be rapid in our experiments and we have not done a full modelling study. However, we have done some back of the envelope steady-state calculations that have established that the maximum contribution from NO<sub>3</sub> oxidation is always likely to be modest in comparison to that from OH. Consider, for example, the ternary experiment after 2.5 hours where O<sub>3</sub> and NO<sub>2</sub> are highest (30

ppb each, see Figure S1). The production rate of  $\text{NO}_3$  will be  $1.98 \times 10^7 \text{ molec s}^{-1}$ . The loss rate to photolysis at our illumination will be around  $0.18 \text{ s}^{-1}$  and to reaction with the remaining cresol, pinene and isoprene at 116, 57 and 41 ppb respectively (see Figure 2) will be 35, 8.8 and  $0.6 \text{ s}^{-1}$ . Ignoring any  $\text{N}_2\text{O}_5$  equilibration (so assuming maximum  $\text{NO}_3$ ), the  $\text{NO}_3$  concentration will be  $4.5 \times 10^5 \text{ molec cm}^{-3}$ . Consumption rates of cresol, pinene and isoprene at this concentration of  $\text{NO}_3$  will be 1.2 %, 0.5% and 0.03% of that to OH at  $1 \times 10^7 \text{ molec cm}^{-3}$ .

- Line 706: *"as much complexity as can be envisaged": this is what you're doing here*

Yes. It became quite clear once we'd started trying to unravel the data and interpret the experiments that it was challenging; though it is undoubtedly of atmospheric importance to address the problem.

- Lines 711 - 712: *True, but you might still get some mechanistic insight*

Agree, though the technical challenge of  $\text{NO}_x$ -free experiments in our chamber are also challenging.

- Line 722: *use of a chemiluminescence  $\text{O}_3$  monitor would help. Not suggesting this to be done in this study, but for broader relevance*

We did try unsuccessfully to use a LO22 instrument for this reason, but suffered considerable technical problems owing to its age. We may try to resurrect it for future experiments, though it is painful.

- Line 725: *yes, OH measurement would be nice, but not trivial*

We recognise the challenges and hence used our approach to attempt to understand the oxidation process.

- 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*

Please see our previous response - we do not have a definitive quantification of the vapour wall loss, which is not the primary focus of the manuscript, though we recognise its importance. No such direct "comparison with the condensation sink" is possible, since the walls and particles are not equally available to the molecules in the chamber. We have experimentally demonstrated that the seed concentrations compete effectively with the walls for the vapours, but agree with the referee's comments that the influence on partitioning could exaggerate SOA differences as stated. There has been a very large effort across multiple chambers to quantify such effects, but this is unresolved. We expand our discussion of this and the need for further work in the revised manuscript, but do not disingenuously claim to resolve the problem.

- 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*

Again, we agree. This is not the primary focus of the manuscript and we cannot claim to resolve this here. It is a problem faced in all chambers and is yet to be resolved. We have raised the problem and its implications in discussion and it must be a firm focus of future work.



- Line 768: *what are Odum curves?*

We have deleted this and referred to the Yield-absorptive mass relationship and the Odum et al. (1996) reference here.

- 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*

We have briefly discussed and added the reference

- Lines 788-792: *see my comment about the yield calculation and exclusion of isoprene above*

Please see our response above

- Line 793: *again, I think a more logical comparison would be "experimental higher than predicted"*

We have reversed the phrasing

- 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.*

We do not have much to add to this discussion point, but have expanded slightly.

- Line 810: *"metastable aqueous electrolyte solution aerosol": what does this mean? Deliquesced? I feel this is being said in an unreasonably complicated way*

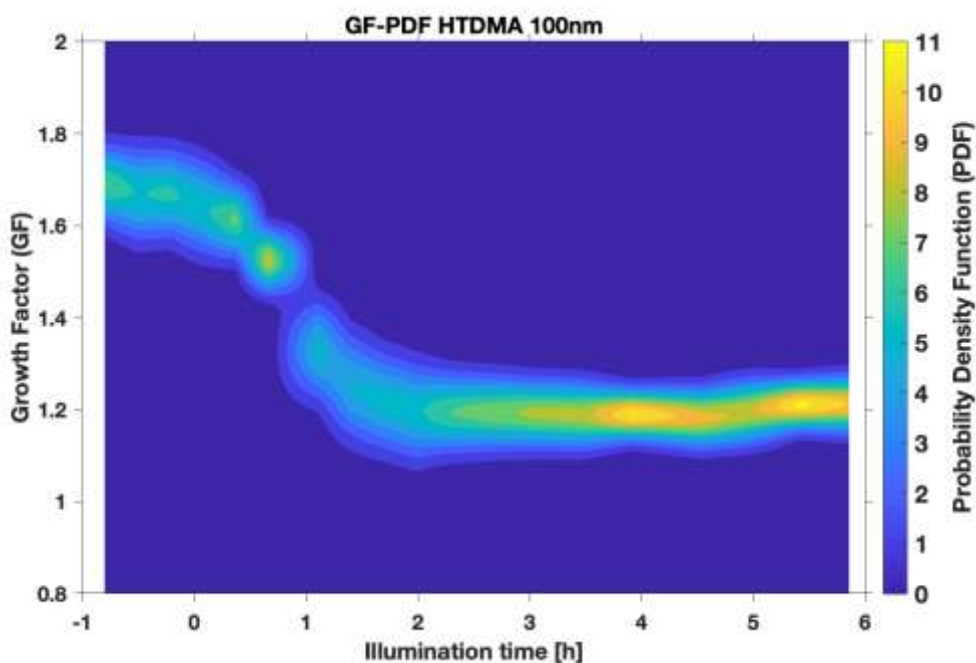
No, the particles have not followed the deliquescence arm of the humidification curve, which shows hysteresis. They therefore have held onto their moisture below the deliquescence point and thus remain in solution at the chamber RH. We do not think there is a simpler way to state this precisely.

- 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.*

Yes, you would get organic mass without seeds, but not as much. Seed particles suppress nucleation because they provide a sink for the vapours that would otherwise nucleate. The measured organic particle mass increases with the presence of seeds when compared with an unseeded experiment, since the seed provides an absorptive mass for the vapours to condense onto rather than being lost to the walls. Until the nucleated particles provide sufficient absorptive mass, they cannot compete with the walls for the vapours as efficiently as injected seeds. We thank the reviewer for pointing out that this is probably not widely known, other than to chamber SOA experimentalists and is likely worth a paper in itself.

- Line 812: *From fig. 13, how can you deduce the particles are internally mixed?*

Taking  $\alpha$ -pinene-isoprene as an example, the time series of GF-PDF of 100 nm particles are shown as below. A single mode of hygroscopicity was observed all through the experiment, indicating an internal mixed aerosol population. Similar results were observed in all investigated systems. An externally-mixed particle population would exhibit bimodality in hygroscopicity, with the inorganic-rich particles growing more. There has historically been some ambiguity in the definition of the term “internally-mixed”. We are using it to mean that all particles in the population, at least at a given time point in the experiment and size, behave the same way, as probed by their hygroscopicity. This is a good indication that the same components are condensing on all particles. For the purposes of the discussion at this point in the paper, it is clear that the inorganic seed is acting as the medium for condensational growth of the particles and that solely organic particles are not being formed. This is not to say that the composition of each particle is the same throughout – the morphology of each particle could lead to differences across the particle with for example, a core-shell structure, a colloidal suspension or individual micellar arrangement. Further work would be required to establish such morphological composition dependence. The particles are metastable solutions, so if the organic compounds are soluble in such aqueous solutions, they might be expected to be well-mixed throughout. If not, the morphology is an open question.



Time series of the probability density function (PDF) of growth factor of 100 nm particles from HTDMA measurement in a characteristic  $\alpha$ -pinene/isoprene experiment. The monomodal distribution represents the internally mixing state.

The rest of the comments on the content in the discussion have been addressed through our decision to move all results that have been more extensively presented in our companion papers into the supplementary information in the form of Figures with extended captions. We then refer the reader / referee to the discussions in each of these studies. The purpose is to point the reader to the associated work where questions raised in our experiments have been more thoroughly addressed. These results are introduced in discussion to state how they are used in these papers to address the scientific points in question. It is far beyond the scope of the current paper to present all these results in detail, but it is important to state that such aspects have been investigated in our experiments. Only brief responses are provided below, since the detail is found in the companion papers.

- 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?*

This is addressed in the companion paper Du et al. (2022) and now presented in the SI.

- 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*

Whilst the  $C_7H_7NO_4$  isomeric contributions do not exhibit obvious differences between systems, the time trend of  $C_7H_7NO_4$  is clearly different. This is now moved to the SI and the discussion and interpretation is addressed in the companion paper Du et al. (2022).

- Line 860: *if these are already reported in detail elsewhere, are they needed in this manuscript?*

All results have been moved to the SI: this summary Figure 11 is not presented in this way in Voliotis et al. (2022) and is briefly introduced here to point at the measurements made and how they aid interpretation.

- 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*

Again, the results and Figure 12 are moved to the SI and the discussion points to the companion paper.

- 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.*

We agree with the referee and this discussion point is now more nuanced, pointing to the balanced argument in the companion paper.

- Line 872: *"three example systems, chosen for...": this should have been said already in the results*

Figure 13, which has been moved to SI is now discussed in terms of being example systems.

- Line 876: *"change in rate of formation": I'm not sure if the rate plays any role, just the formation in general*

We agree that the OA/inorganic ratio is the key controlling factor and the rate just determines when a particular ratio occurs.

- Line 902-903: *are the filter results so essential as to dictate the concentration regime?*

At the current time, only offline techniques are powerful enough to provide structural information. If clear mechanistical information is to be the goal of such studies, the detection limit of offline mass spectrometry methods currently dictate the concentration regime we can work with. Improved resolving power of online techniques may alleviate this restriction, enabling mechanistic information under lower concentration regimes.

*- Lines 930-931: I don't think this is the case*

Please see our previous responses. The yield is ambiguous – the VOC consumption is in the denominator of the yield and whether all VOCs consumed are considered, or just those acting as SOA precursors, directly influences the reported yield.

*- Line 940: "will depend on the rates": I don't think it's evident that it would be rate dependent*

This has been change to refer to the organic to inorganic ratio as the controlling factor, whilst the formation rate of SOA in each system determines the time at which such an organic to inorganic ratio occurs in a particular system.

*A list of technical comments*

We thank the referee for these, which are all addressed in the revised manuscript

*- 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  $\alpha$ -pinene had all of the 1, 1/2 and 1/3 experiments

- Line 633/Fig. 11: dot area or diameter is sized?

Dot area is sized, this has been clarified in the updated caption, now found in the SI.

- 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?

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