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 if 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 a-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.

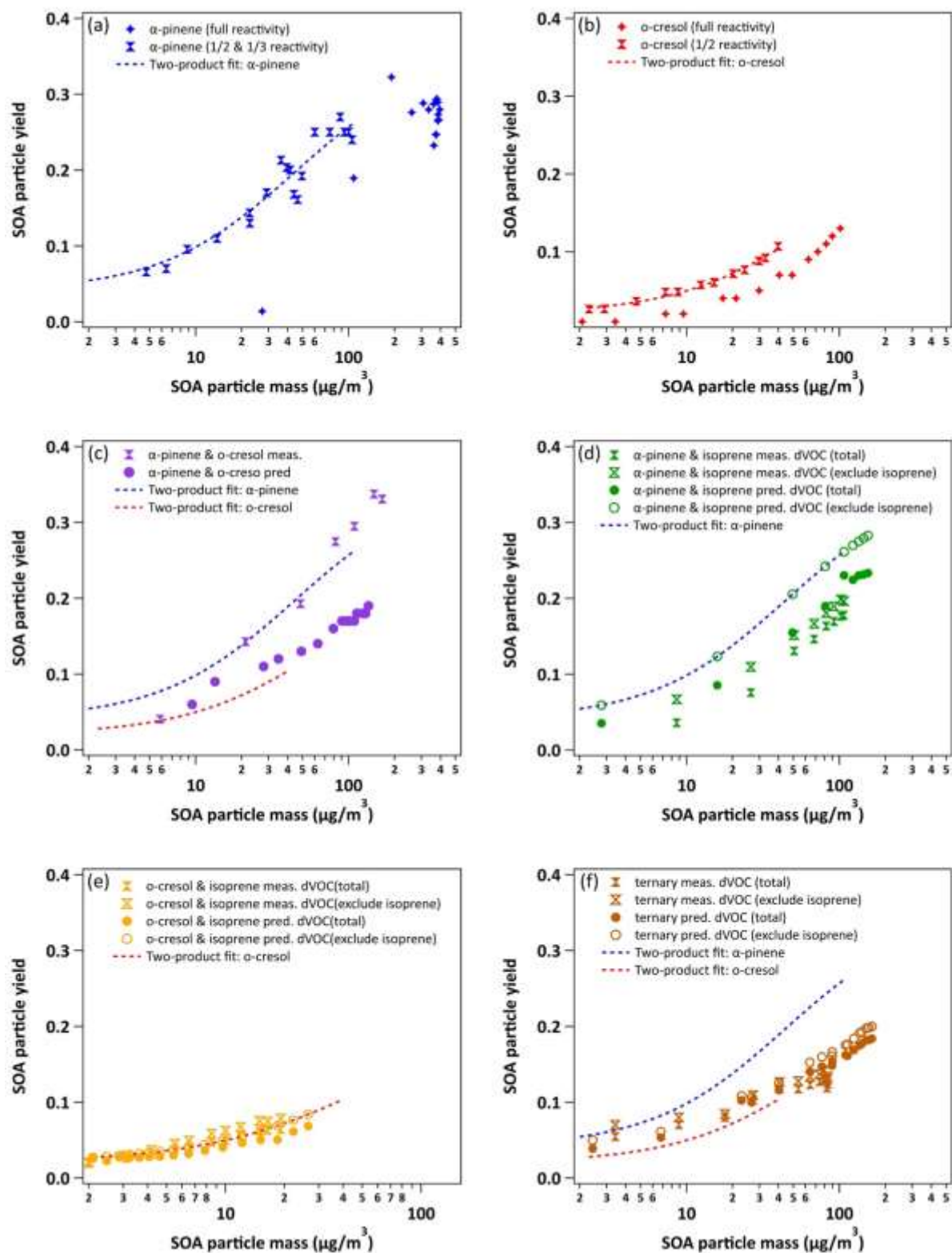



Figure 5. Yield data for selected representative experiments in all systems (with two-product yield curves for α-pinene and *o*-cresol single VOC experiments). Panel a) shows the measured/predicted yield versus SOA mass in the single VOC α-pinene system, Panel b) single VOC *o*-cresol system, Panel c)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

pinene / *o*-cresol mixture, d) the binary α-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.

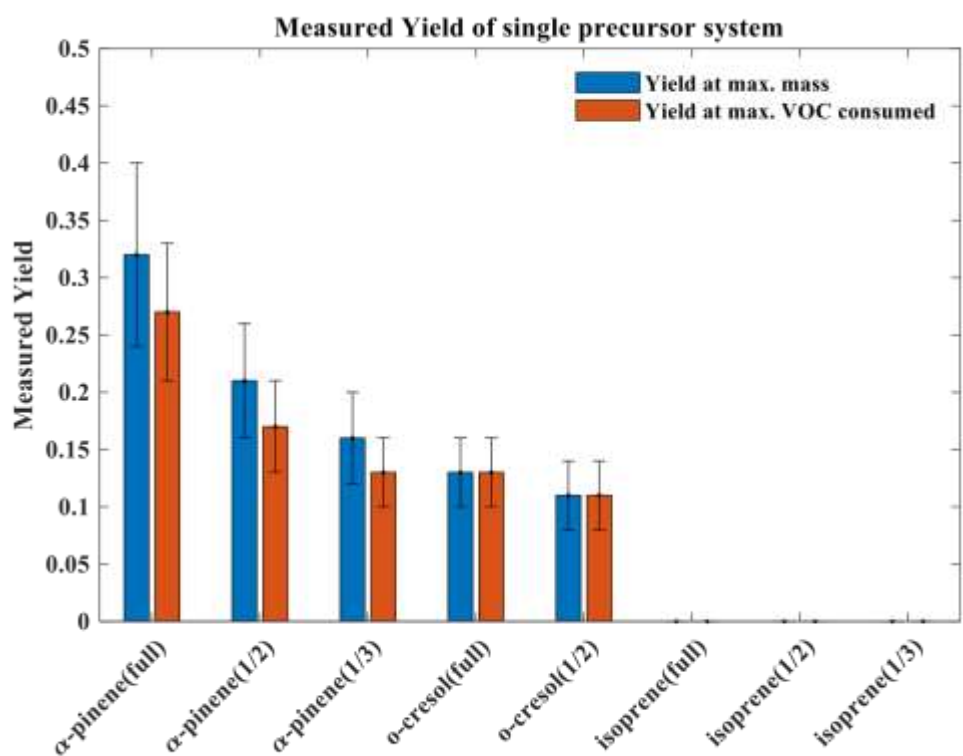



Figure 5: Measured yield for all single precursor system calculated at maximum particle mass and maximum VOC consumed

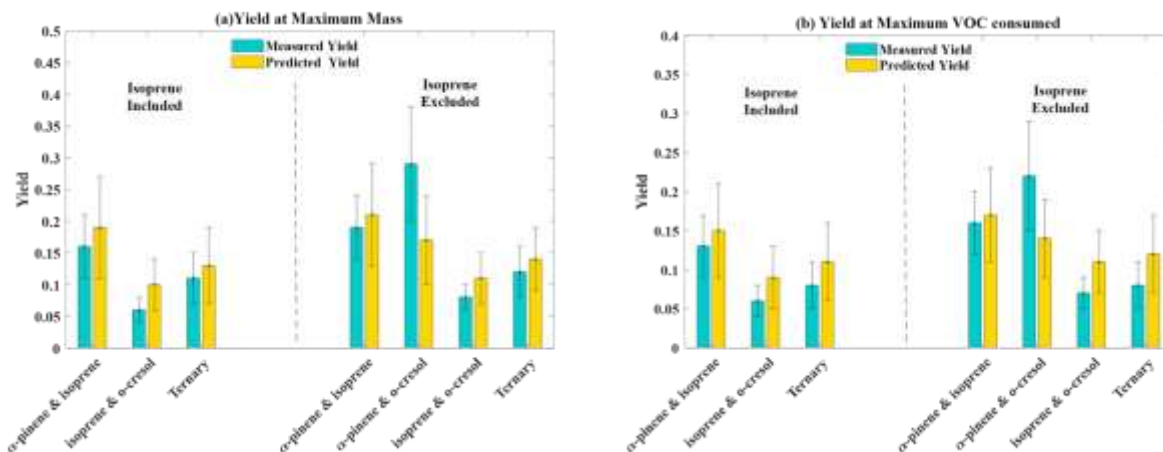



Figure 7: (a) Measured and Predicted yield for all mixture precursor system calculated at maximum particle mass; (b) Measured and Predicted yield for all mixture precursor system calculated at maximum VOC consumed. For mixtures containing isoprene, which had zero yield on the neutral seeds injected, 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 1.4μg 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 ± 1σ uncertainties of predicted △SOA and measured △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 a-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_2-RO_2 accretion product formation and their potential significant contribution to the SOA particle formation and growth, showing that presence of isoprene inhibited α-pinene C_{19-20} dimer formation and increased the C_{15} 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-autoxidation-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 Atknison 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 airmasses. 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 α-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 NH3? Does this have any other implications

There have never been any experiments in the chamber with addition of NH3 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?

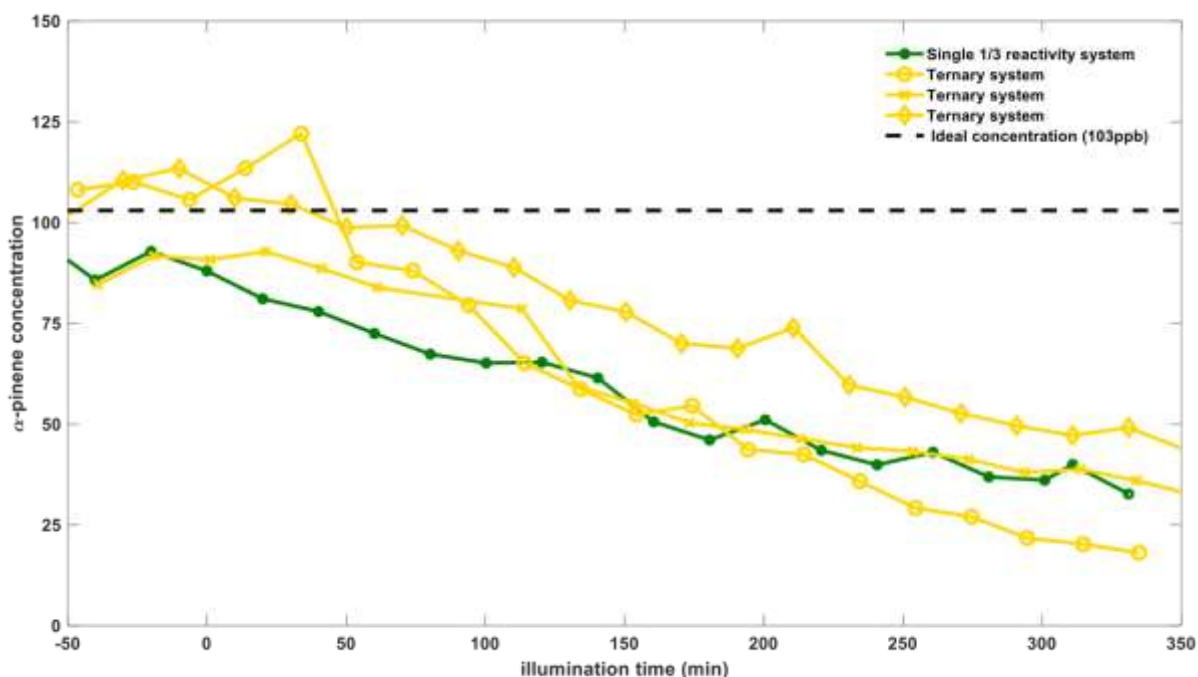
This is in Shao et al. (2022a), citation added.

- 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 a-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 a-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 ±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 α-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 a-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 α-pinene and o-cresol precursors respectively, were expected to provides 10 to a few 100 μgm^{-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+HO2 flux relate to this? Isn't that a sink for HOx? A schematic figure, or at least a through explanation on this, would be good

NO+HO2 produces OH, so not a net loss of HOx – it is a well-known coupling between the HOx and NOx cycles in standard VOC degradation in the presence of NOx. 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 NOx and O3

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^{-3}, 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 NO2 + 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$_2$, NO and O$_3$ 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$_3$ measurement by UV absorption was influenced by UV absorption by *o*-cresol and O3 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 O3 slopes be the same? If something, I would imagine NO to be shorter lived, so its slope should be smaller than that of O3. 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 NOx from the laboratory levels at ambient concentrations at our high inlet flow rates, despite passing through our Purafil filter. We never aim to conduct NOx-free experiments and work with a few ppbv NO background. NO, NO_2 and O_3 initially move towards the photostationary state, with O_3 being produced from NO_2 photolysis. The VOC oxidation then leads to additional ozone production as VOCs are consumed through the NO reaction with HO_2. The system then attempts to attain the continually evolving photostationary state. OH is formed through the photolysis of O_3. In the case of an unsaturated biogenic VOC, there is O3 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 NOx and O_3.

- 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:NOx 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

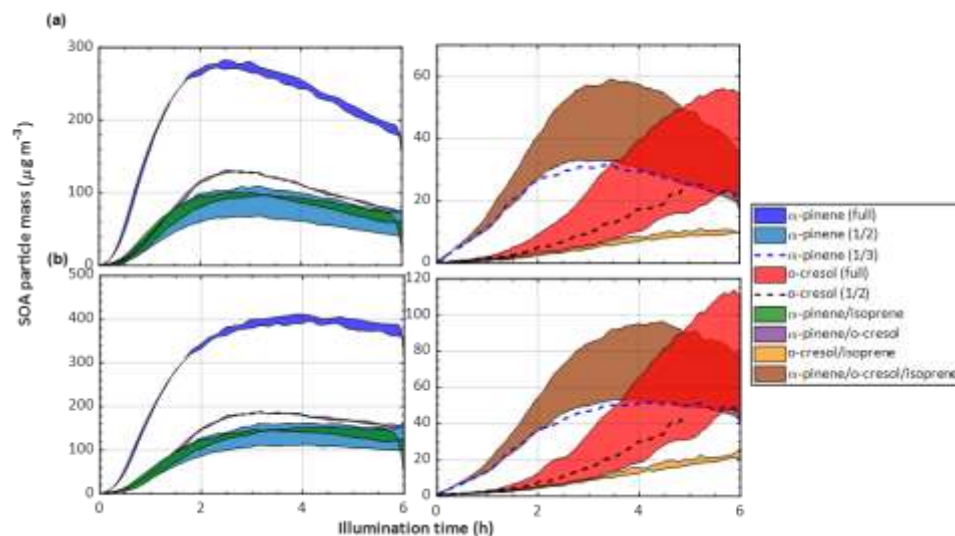
- Lines 416-417: add reference

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 supple. Could the whole paragraph be moved to the supple?

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 α-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/Fig5: 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.

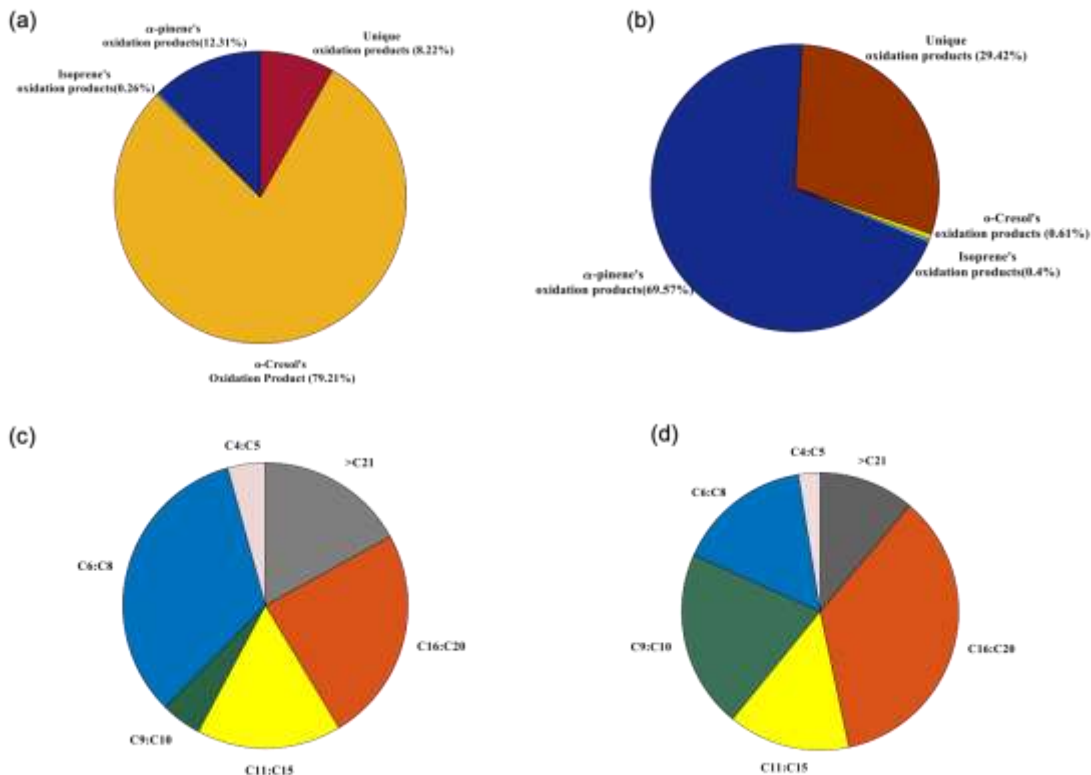
A note to this effect is made in the revised sentence.

- 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 α-pinene (a1 and a2), *o*-cresol (b1 and b2) and mixed α-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 α-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).'

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.

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).

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 (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 (α-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 α-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

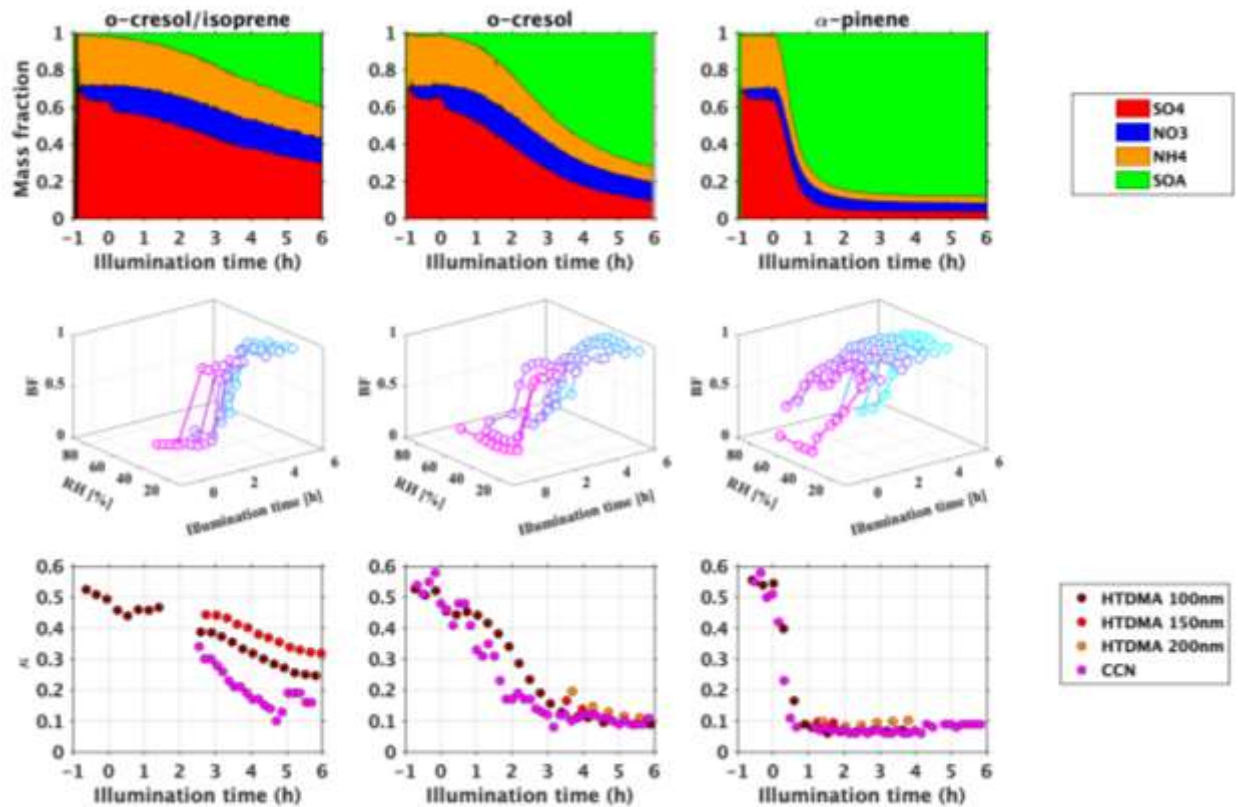
Yes, we were imprecise. The sentence has been rephrased to: "It is clear that the organic to inorganic ratio, controlled by the amount of SOA formation, determines the physical behaviour of the particles."

- 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 α-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.

Values of Leighton ratio below 1 could arise from a wall source of NO. Alternatively, errors propagated from the determination of jNO_2 from actinometry experiments and measurements of NO, NO_2 and O_3, as well as the heterogeneity of the j_{NO2} 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.

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.

This was already directly discussed in Section 5.1

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_3 below.

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

Continuous NO_3 injection is performed by preparation of frozen pure N_2O_5 and flowing N_2 across the headspace. We aborted a project using this technique on these mixtures at the beginning of Covid lockdown. Watch this space.

Indeed, the production rate of NO_3 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_3 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_3 ond NO_2 are highest (30

ppb each, see Figure S1). The production rate of NO_3 will be 1.98 x 10^7 molec s^{-1}. The loss rate to photolysis at our illumination will be around 0.18 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 s^{-1}. Ignoring any N_2O_5 equilibration (so assuming maximum NO_3), the NO_3 concentration will be 4.5 x 10^5 molec cm^{-1}. Consumption rates of cresol, pinene and isoprene at this concentration of NO_3 will be 1.2 %, 0.5% and 0.03% of that to OH at 1 x 10^7 molec cm^{-3}.

- Line 706: "as much complexity as can be envisaged": this is what you'te 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 NOx-free experiments in our chamber are also challenging.

- Line 722: use of a chemiluminescence O3 monitor would help. Not suggesting this to be done in this study, but for broader relevance

We did try unsuccessfully to use a LOZ2 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 a-pinene OH/O3 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.

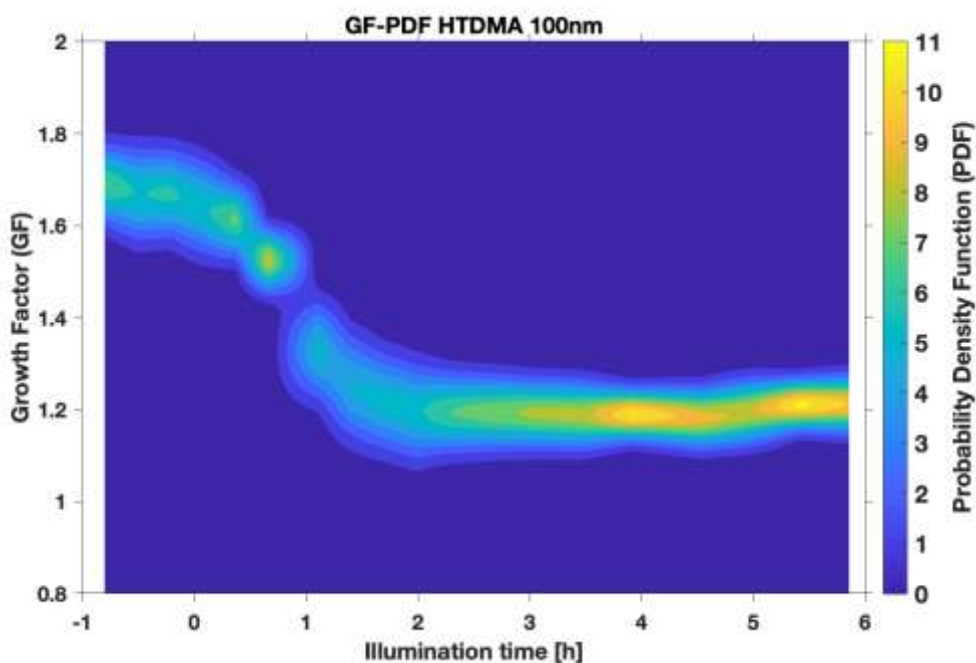
- Line 810: "metastable aqueous electrolyte solution aerosol": what does this mean? Deliquesced? I feel this is being said in an unreasonably complicated way

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 a-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 α-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. The 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 α-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 dont' 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 a-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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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 2 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):

Review of "Chamber investigation of the formation and transformation of secondary organic aerosol in mixtures of biogenic and anthropogenic volatile organic compounds" by Voliotis et al.

This paper reports on the initial findings of a series of laboratory experiments conducted in the Manchester Aerosol Chamber to examine the behavior of oxidation of mixed biogenic and anthropogenic VOCs to determine deviations from expectations of the yields of secondary organic aerosols, and possible reasons for such deviations. The paper presents the experimental design and selected results in a logical sequence that is generally easy to follow and understand. This reviewer found the topic interesting with cleverly designed experiments and insightful interpretation of the wide array of measurements. This paper represents a valuable contribution to our understanding of the details of oxidation of VOCs as related to production of aerosols under various conditions. The McFiggans group has led the community in the interesting area of mixed biogenic-anthropogenic VOC oxidation and production of SOA. This paper, and the ones to follow about these experiments, continues that legacy.

On the organization of the paper, after the introductory material, the figures are discussed along with aspects of the study (starting on line 375). The last figure (13) is referenced on line 650. Then in the discussion, the figures are discussed again (starting on line 674) in order. This reviewer suggests that the authors say everything to be said about the figures in the first pass, and then shorten the discussion to only the key points of the study. This is only a suggestion for the authors to consider.

We thank the reviewer for this suggestion and agree that the organisation could benefit from attention. We have partly taken the referee's suggestion on board but have more radically changed the paper to present all the results from the companion papers along with the associated Figures, into the supplementary information. This leaves them only to be referred to in the discussion section along with some discussion of the expansion of the interpretations in each paper. This is because of the progress made in the reviews and publication of the companion papers and the requirement to maintain the focus on the key new points in the current paper.

General comments.

While this review found the paper overall well-written and organized, there were some instances of jargon usage and awkward wording. These are pointed out in the specific comments. In the discussion and conclusions, the interference of VOCs in the measurement of ozone was noted. Had this been recognized earlier, an alternative method of measurement could have been employed (e.g. reverse NO chemiluminescence). Perhaps this should be briefly mentioned. It is also important to note that the Thermo 42i NOx analyzer has significant interference from reactive nitrogen compounds other than NO_2 in the NOx

mode due to the converter employed in this instrument. This should also be mentioned, perhaps in a footnote of Table 2.

These are well-noted points. We became aware of the ozone interference during the measurement campaign and hurriedly attempted to deploy an old LOZ-2 ozone analyser using chemiluminescence with eosin-Y dye for all *o*-cresol containing experiments. Unfortunately the instrument suffered problems and useful data were not recoverable. Concerning the NOy interference, we have noted this in the revised text.

Specific comments.

Line 60. In the first mention of VOC:NO$_x$ ratio, indicate that it is a ratio of mixing ratios (in other words, a molar ratio). This is important because is could be a ratio by mass.

We have clarified this and included ppb/ppb in the text.

Line 61. It is not clear what is meant by "less mechanistically". Perhaps use different terminology.

We mean that the exact chemical components acting as precursors and the mechanistic interactions in their degradation chemistry influencing the components partitioning to the particles are seldom considered. We have tightened up the language here.

Line 66. What is meant by "numerous representations of atmospheric SOA"? Consider different wording.

Rephrased to "numerous ways of representing the formation and transformation of atmospheric SOA"

Line 129. Suggest "use these metrics to quantify interactions in the oxidation of VOC mixtures leading to changes in SOA formation compared to those expected based on..."

Agree – changed.

Line 132. Suggest "use a suite of online and offline measurements...and the resulting properties of potential atmospheric significance."

Agree - changed

Line 141. Perhaps reword or add additional text to explain "...makes a comprehensive programme intractable."

This has been both reworded and expanded a little.

Line 151-2. Suggest "...study of a random mixture is expected to yield novel, but complex results. Thus, care is required to fully interpret information from such studies." ...or something similar.

Yes – this sentence has been simplified.

Line 159-160. This reviewer is not convinced that it is established how NO$_x$ affects SOA formation yields dramatically. While some studies have shown this, others are less convincing. It is not even obvious what the slope of the yield versus NO$_x$ function is. Suggest softening this assertion.

The NOx dependence is indeed ambiguous and we have recognised the contradictions in the literature in the revision. The mechanistic pathways during VOC oxidation during which SOA particles are formed are undoubtedly influenced and this is really all we were saying. It was in the light of this that we were contextualising our choice of VOC:NOx ratio. The assertion has been softened.

Line 162. The sentence that begins "Truly low NO$_x$ regimes do not occur widely in the ambient atmosphere..." could certainly elicit discussion. It depends on the definition of "low NO$_x$" and "widely", which have not been presented here. There are certainly remote regions where the NO$_x$ is very low (10s of pptv), but it probably is hard to argue that such locations are widespread. Suggest softening this assertion. Since the use of low and moderate NO$_x$ levels are used in the paper, perhaps somewhere consider quantifying what is meant by these descriptors.

We have balanced and softened the assertion.

Line 182. Suggest changing "...sort of atmosphere that..." to something else that is clearer, such as "...level and mixture of atmospheric components that are employed to approximately represent a given atmospheric situation."

Clarified our sloppy language.

Line 188. Several places in this paper use future tense, when present tense is more appropriate. This is one of those places. Suggest "...of the current approach is of considerable interest."

We have checked our tenses throughout.

Line 196. The use of ammonium sulfate particles is mentioned and justified, but the reason for this particular choice is not mentioned. Perhaps include a bit more information.

We're not completely sure of the additional information that the referee is asking for, but we have added a little more justification in terms of ammonium sulphate being one of the most abundant electrolytes in the atmosphere and a component most easily and reliably determined by online instrumentation such as the AMS (to contrast with, for example, sodium chloride).

Line 203. Suggest "Ammonium sulphate solutions are nebulized into...".

Agree – changed.

Line 210. Table 2 is referenced here, before Table 1. Suggest renumbering and reordering the tables. It is stated that the measurements are "state-of-the-science". While this is true for some of the instruments, it is not universally true. Suggest rewording this sentence.

We have removed reference to table 2 at this point and the statement of the instrumentation being "state-of-the-science …throughout".

Line 211. Time resolution of the measurements is mentioned. Perhaps include the time resolution or integration time in the instrument table.

Table 2 has been updated with the time resolution as follows:

Table 2: List of instrumentation employed over the course of the study

Instrument	Model	Measured parameter	LOD/ range	Time resolution
Dew point hygrometer	Edgetech (DM-C1-DS2-MH-13)	Dew point	$-20 - 90 \pm 0.2\ ^\circ C$	1s
NOx analyser	Thermo 42i	NO, NO_2	0.5 to 1000 ppb	10s
O_3 analyser	Thermo 49C	O_3	0-0.05 to 200 ppm	10s
Water-based condensation particle counter	TSI 3786	Particle number	$<10^7$ p/cc	1s
Differential mobility particle sizer	Custom-built[a]	Particle size	40-600 nm	600s
Filter collector	Custom-built[b]	Particle collection for offline analysis		n.a.
Condensation particle counter	TSI 3776	Particle number	$<10^7$ p/cc	n.a.
Scanning mobility particle sizer	TSI 3081	Particle size	10-1000 nm	120s
High-resolution aerosol mass spectrometer	Aerodyne	PM_1 non-refractory particle composition	$>0.05\ \mu g\ m^{-3}$	60s
Iodide chemical ionisation mass spectrometer	Aerodyne/Tofware	Oxygenated VOC	LOD >60 ppt; Mass resolution 4000 Th/Th	0.25s
Filter Inlet for Gases and AEROsols	Aerodyne/Tofware	Particle composition	$>10^2$ ng	n.a.
Semi-continuous gas-chromatograph mass spectrometer	6850 and 5975C Agilent	VOC concentration	>0.4 ppb	1200s
Liquid chromatograph – orbitrap mass spectrometery	Dionex 3000, Orbitrap QExactive, ThermoFisher Scientific	Particle composition		n.a.
Hygroscopicity tandem differential mobility analyser	Custom-built[c]	Hygroscopicity	20-350 nm	600s
Cloud condensation nuclei counter	Droplet measurement Tech (model CCN-100)	CCN activity	$>6 \times 10^3$ particles cm^{-3} at SS:0.2%	600s
Thermal denuder	Custom-built[d]	Volatility	Temperature range: ambient – 200°C	n.a.
Three arm bounce impactor	Custom-built[e]	Particle bounce	20-500 nm, $< 10^4$ particles cm^3	90s

[a]Alfarra et al. (2012)
[b]Hamilton et al. (2011)
[c]Good et al. (2010)
[d]Voliotis et al. (2021)
[e]Liu et al. (2017)

Line 215. It is a little unclear what is meant by "collection of sufficient mass" in this context. Perhaps add a few words to indicate that the detection limits for aerosol components are enhanced by maximized the total mass of aerosol collected.

Added. This is indeed the point.

Line 234. It is not clear what is meant by "...throughout the photochemistry...". Suggest rewording.

Reworded to "as it transforms throughout the experiment".

Line 236. Suggest rewording "...characterization of the transformations of the oxidation products...". The oxidation products are the result of oxidant attack on the primary VOCs, perhaps in multiple generations, so oxidation products can be oxidized, but it is not clear what the point is here.

Agree – we quantify the changing concentrations of oxidation products that may partition between phases.

Line 237. It is unusual to use the term "payload" for instruments used in a ground based laboratory or field study. It is usually reserved for aircraft studies. Suggest using "suite" or some other term.

Changed to "suite"

Line 251. Suggest "The biogenic VOCs that were chosen were α-pinene and isoprene..."

Changed

Line 256. Suggest "This means that the initial amounts are added in a α-pinene : isoprene : o-cresol ratio of 309 : 164: 400 based...".

Changed

Line 266-7. Suggest rewording this sentence. This appears to be a disjoint collection of sentence fragments. It might be easily fixed by a couple of transition words.

Tried to make it a bit more fluid

Line 273. Change to present tense: "non-linearity leads to changes in the...". Line 277. Could eliminate the word "Ambient...".

Tense changed

Line 287. Suggest "...mimic a specific atmospheric region, but more to explore...".

We use "atmospheric chemical regime" to capture not only geographical region, but seasonal / diurnal temporal variability and are not sure that this suggestion captures what we intended.

Line 289. I'm not sure what is mean by "neutral seed experiments". Suggest rewording.

Changed to "non-acidic".

Line 290. Suggest "...particularly acid catalysed reactions."

We are not sure that this is correct so have revised to "…condensed phase reactions, particularly those that are acid catalysed"

Line 298. Suggest replacing "space blanket" with "Mylar film". Also suggest "...homogenise the light intensity throughout the chamber."

Changed

Line 302. Suggest "...transmit light up to 100% above 305 nm."

Changed

Line 318. Suggest "...is conducted using full illumination without the UV filter on the arc lamps and using ppm levels..."

Changed

Line 322. It is not obvious why the term "stock solution" is used and why the concentration is given, since the sentence indicates that the concentration is changed to control the seed concentration. Suggest rewording.

Reworded

Line 325. Suggest rewording the phrase to read "...by irradiating the chamber mixture for the selected conditions of VOC and NO$_x$.

Reworded

Line 327 and 329. It appears these are almost the same sentence. Suggest eliminating one of them. It is possible that all the text in lines 327-330 could be replaced by "The correction for the interference by o-cresol is determined by the ozone instrument signal measured before the experiment began and using the change in o-cresol concentration determined by the CIMS instrument."

Deleted the repetition

Line 345. Suggest beginning this sentence with "The instrumentation includes: a high-resolution..."

Reframed the sentence as suggested

Line 351. Suggest "...of the online instrumentation was changed after several hours of reaction to cycle..."

Changed

Line 353. Suggest "...Table 2 provides the list of instrumentation...". Also change table number as per previous suggestion.

Removed the earlier reference rather than renumbering

Line 357. Suggest adding more detail about the "actinometry and off-gassing experiments". At least say what parameters were determined, and maybe briefly describe how they are done. Also include references as appropriate.

We've referenced Shao et al. (2022a) and briefly expanded the sentence.

Line 362. Suggest "...in the MAC forms O_3 which rapidly establishes the photostationary state...".

We've subsumed much of the text into a methodology section which is now in section 2 and this sentence has been revised in this section.

Line 367. It seems that the phrase "at a given OH" could be removed. If there is isoreactivity, then it doesn't matter what the OH is, correct?

True. What we had meant to state was "… at *any* given OH concentration" – it does not state that the OH will be the same between systems.

Line 369. Suggest "...concentration), in practice the loss rate of each VOC..."

Changed

Line 371-3. The formation of HONO on chamber walls and release to the gas phase is well-known and has been studied for a long time. Suggest a more recent reference and perhaps a bit more discussion for those readers that might not be familiar with this issue.

A briefly expanded discussion has been provided in the revision

Line 379. Figure 1 x-axis label. Suggest something like "Illumination time (h)".

We agree that "lights on" is a bit parochial, so have taken this suggestion

Lines 382-395. With the discussion of the photostationary state and the Leighton ratio, in principle you could calculate the HO_2+RO_2 concentration that explains the observed ratio. Not discussed were the instances where the ratio is observed to be less that unity. Suggest adding some text to expand this discussion, or alternatively to eliminate the topic completely.

We include some discussion of this from line 682 in the original manuscript which we have expanded in the revision. The values below unity imply a local source of NO. This may arise from a wall NOx source, but must be the subject of further investigation.

Line 420. Suggest "...not all VOC were consumed...". This is because VOC is plural. This reviewer prefers VOC for singular and VOCs for plural, but this is not widely accepted.

We are in agreement with the reviewer in preferring pluralisation to VOCs, but will defer to convention. We have changed all occurrences to reflect this.

Line 431. Suggest "The same colour scheme as in Figure 2 is used."

Changed

Lines 440-1 and 443. The terms "particle mass" and "SOA particle mass" are used interchangeably in the first sentence, but this is not strictly correct. It is not really necessary to include "particle" with SOA, since SOA includes "aerosol". "SOA mass" should suffice in this discussion. Note that "particle mass" and "SOA particle mass" are used incorrectly (meant to mean SOA mass, but strictly meaning total aerosol mass) throughout page 18 (and Figure 4 caption), and perhaps elsewhere in the paper. Please search for this term and correct its usage.

We agree with the first part of the referee's comment – particle mass is not SOA particle mass, since it will include inorganic. However, the particle yield does not include the gas phase components, so the yield should be SOA particle mass / VOC consumed. It should not be Total SOA mass (including gas mass) / VOC consumed. We have checked all usage and made it consistent with this definition, which we contend is correct (and consistent with previous usage).

Lines 443-444. It is difficult to see that that this sentence is a list of possible alternatives for calculation of yields. Perhaps number (1, 2, 3) of add a letter (a, b, c) to the various options, or change the wording of the first part to indicate that various options are coming in the rest of the sentence, for example "...the yield is reported as a single number that could be calculated from data at various times in an experiment, including at maximum SO2 mass, ..."

We have broken down the sentence to make it clearer

Line 480. The term "referenced" is used, but perhaps "compared" would be better. This applies at many places in the paper.

We had used the term "referenced" since it is intended to specify a reference baseline. We agree that compare is more precise, and use "compared to the baseline mixture without isoprene" etc…

Line 481-481. The nomenclature for the various yield calculations can make the sentence grammar confusing. This sentence is an example. The use of "yield at maximum mass" might be better with a symbol (such as Y_{MM}) which is defined somewhere and then used in the discussion. Likewise with the other types of yield calculations (e.g. Y_{MVC}).

We agree and have adopted this suggestion

Line 482. Suggest "The uncertainties in SOA mass yields were calculated by...". Also, this implies the uncertainties shown in Table 3 are 1σ, but this is not explicitly stated.

We disagree with this, since SOA does not include gaseous mass, so retain "SOA particle mass yield"

Table 3. In an earlier table, a "-" indicated missing data. What does it mean in this table?

The '-' also indicated missing data in Table 3. Table 3 has been replaced by the figure as shown in Response to Referee 1.

Line 485. In this sentence "organic mass" is used to mean "SOA mass". Suggest being consistent in the terminology throughout the paper.

Yes, the terminology should be consistent throughout the whole paper with "SOA particle mass".

Also, this sentence is confusing, because it apparently refers to equation (4), but equation (3) is shown first. Suggest reordering the text and equations to make things clearer. The symbols in both equations need to be defined.

Equation 3 has been moved ahead of the Figure that replaces table 3, immediately after the introduction of equation 3 and all terms have been defined.

The term "additively combining" means simply that the predicted yield is the mass of SOA for each component determined from the single VOC experiments at the same amount of VOC reacted divided by the sum of the amounts of each VOC that reacted. It may be that the sentence in line 485-6 is meant to say this, but it is a bit confusing. Consider rewording.

The referee is correct – it has been reworded to clarify "Figure 5 shows "predicted" yields for the mixtures, based on the sum of the SOA mass determined from the single VOC experiments divided by the sum of the amounts of each VOC that reacted according to eq. 4"

Line 490-3. This sentence is also confusing. Are the two-product fits referred to from equation 3? Perhaps more information is needed to clarify this sentence. Also, the term "particle mass" is used again.

The sentence has been rephrased to: "The parameters (alpha1, alpha2, Kp1, Kp2) from the two-product fit by eq.3 from the single VOC half- and third-reactivity experiments were used to generate a yield-mass-ΔVOC look-up-table. This look-up table is then used to predict the SOA particle mass from each VOC with known VOC consumption in the mixed systems."

Line 528. It is not clear what is meant by "decremental decay" in this context.

This means the stepwise decrease, time interval by time interval – in the same way that an incremental build up would be used to describe a stepwise increase.

Page 23. There are several instances of "particle mass" on this page.

Now all SOA particle mass

Line 539. Suggest "Measured (15% error) and reconstructed decays of (a) isoprene and (b) α-pinene in...".

Changed

Line 540. Suggest "In each case, the initial decay of the VOC due to reaction with ozone was calculated based on the initial concentrations of O_3 and the VOC along with the appropriate reaction rate coefficient."

Sentence rewritten to clarify

Line 548-549. Suggest "...yields owing to the differences in the tendencies of oxidation products from reaction with different oxidants to condense."

Agree - changed

Line 551. Suggest "...AMS total signal at m/z values of 44 (f_{44}) and 43 (f_{43}) to represent more or less oxygenated contributions, respectively, to the SOA mass."

From this point onwards to line 660, all Figures and results have been moved to the Supplementary Information, with much of the text subsumed into extended Figure captions. We have responded to the comments here, but most of this is now in the SI.

Line 554. Suggest "...in all systems explored in this study."

Agree. Included in expanded caption

Line 564. It is not clear what is meant by "...more oxidized and higher...". Suggest rewording.

Agree, now "…more oxidised products with higher f_{44}"

Line 576. Suggest "A more thorough study of the aerosol composition using analysis of the high resolution AMS is data is the...". Not all readers will be familiar with what "high resolution" means in this context, so somewhere define that it is high mass resolution (as opposed to high time resolution or some other type).

Agree – now state "high mass spectral resolution" at first use.

Line 587. Suggest "...and mixed α-pinene / o-cresol systems...".

Changed

Line 599. Suggest defining "-ve" and "+ve" ionization modes here or elsewhere in the paper.

-ve and +ve replaced with negative and positive throughout

Line 601. Suggest "...phase reactions cannot be determined from these...".

Changed

Line 606. It may be obvious but suggest defining the term "unique-to-mixture" compounds somewhere.

These compounds are now solely referred to by the description "compounds uniquely found in the mixtures"

Line 616. Suggest *"Panel (a): Amounts of $C_7H_7NO_4$ isomers products in o-cresol systems as measured by...of each experiment in this study; and (b) time series of total aerosol phase $C_7H_7NO_4$ (all isomers) from...". Also, do these plots indicate inconsistency between the two measurements? If so, this should be discussed in the text.*

Changed to 'Panel (a): Amounts of $C_7H_7NO_4$ isomers products in *o*-cresol systems as measured by LC-Orbitrap MS analysis of each experiment in this study; and (b) time series of total aerosol phase $C_7H_7NO_4$ (all isomers) from FIGAERO-CIMS. The peak area of each compound/isomer was normalised to the corresponding total peak area of all detected compounds from LC-Orbitrap MS and FIGAERO-CIMS, respectively'. The figure is shown in Figure S10.
The reasons behind the different chemical compositions between the two instruments are discussed in Du et al., (2022): 'there are a number of factors that could result in the differences in the composition, including thermal desorption of SOA in the filters or the selectivity and sensitivity of instrumental ionisation methods toward compounds (Stark et al., 2017; Mehra et al., 2020; Voliotis et al., 2021) and possibly differences in the limits of detection of the instruments as suggested by the reviewer. It is not possible to attribute the differences in composition to a specific cause in our experiments, but this should be the focus of future work.'

Line 625. Suggest *"...found predominately in the aerosol phase (i.e. exhibiting low volatilities)."*

Changed

Line 632-3. *It is not clear why the data from the end of each experiment was presented in Figure 11. Would it not be better to either show time series or to show data at the peak of the SOA yield. Suggest adding some explanation in the caption or the text why this approach was taken.*

The time evolution of the O:C and nC (and perhaps the OSc) is indeed interesting and is described in detail in an upcoming publication (Shao et al., 2022; in preparation). Towards the end of each experiment, most of the systems tended to be more stable, i.e., the formation rate of SOA particle mass < wall loss rate, indicating less rapidly changing chemistry (see Fig. 3). Therefore, the data from the final cycle of the FIGAERO-CIMS in each experiment were chosen as a reference. The caption has been extended in the SI

Line 656. Suggest *"The evolution of these properties for all the systems in this study are discussed in detail..."*

Changed

Line 666. Suggest *"The control of photochemical conditions in the VOC mixtures studied here is challenging."*

Changed

Lines 666-673. *In the discussion of the challenges with different reactivities of OH and O_3 for the various VOCs, you might want to discuss the philosophy of adding oxidant scavengers. For example, a carefully selected alkane could be used to scavenge OH and then O_3 reactions could be studied in isolation. The (as stated elsewhere in the paper) an alternative OH source that doesn't make ozone could be used to study*

OH reactions separately. Good understand of single oxidant systems could then be followed by those with multiple oxidants. Clearly, in a study such as this, one must be careful with such approaches, but it would be helpful for the reader if the topic is discussed.

This opens a philosophically interesting set of discussions. Careful selection of an alkane can indeed be used to scavenge OH. However, the peroxy radical product will act as a potential termination partner for peroxy radicals formed from SOA particle precursor oxidation. This involvement of the products of scavenger oxidation in the formation of SOA particles makes the impacts on their formation in mixtures quite challenging. Additionally, the reference baseline for the mixture yield would need to be established – is the VOC consumption included in the yield. This is precisely the discussion we opened with respect to isoprene in the systems we have reported. We are sure that there is insight to be gained by isolation of the oxidants, but are not sure of the best way to do this. We have included a brief section further raising these points in the amended discussion.

Lines 681-2. Need to define "+ve" and "φ".

+ve replaced with "positive", "ϕ" now "Leighton ratio, ϕ"

Line 690-694. In this discussion, it is clear that the chemistry of SOA formation needs to be understood over the range of oxidants studied: from pure OH to pure O_3. With such understanding, studies in specific systems of OH : O_3 can potentially be compared. It is complex, but as with other chemical systems, the detailed mechanistic understanding must be developed before results from complex systems can be interpreted. Did you consider trying to develop a detailed model (using MCM with specific additions, for example) to try and constrain the mechanism responsible for the observations?

We have thought hard about the means to constrain the mechanisms. It became apparent throughout the campaign that the differences in the oxidants were substantial from one mixture to another. The experimental design to move from one oxidant to another is quite different and out of scope of our study. We agree that the detailed mechanistic understanding must be developed before results from complex systems can be interpreted, but it has never been demonstrated that this is the case – for example, that yields in mixtures are not additive, or composition changes when combining precursors, for example. This is the starting point of our study and the mechanistic interpretation will necessarily follow from subsequent experimental campaigns. This is going to be a long programme of study…

Line 700. Suggest "…derived RO_2 must be considered."

Changed

Line 702. Suggest "…reaction with NO_2 can be quite complex."

Changed

Page 33 and 34. In the discussion of the complexity of such systems as in this study involving multiple oxidants with reactivities of VOCs toward the oxidants changing with time, it should be recognized and pointed out that oxidants can be measured. Indeed, you have direct measurements of O_3 (albeit with the o-cresol interference) and direct OH measurements are possible. Such measurements seem critical to the success of studies such as the one presented in this paper. There are alternative methods (such as decay

of a VOC that only reacts with OH; VOC decay mentioned in line 719) to determine oxidant levels. Also, OH levels can be minimized by addition of compounds that do not affect aerosol yields, such as CO. Thus, it is conceivable that many of the complex issues discussed on these pages could be managed by careful design of experiments, including the addition of further experiments. Additionally, it is conceivable that compounds other than those selected might be better choices for a mixed oxidant system. For example, selection of an aromatic compound with an unsaturated side chain might be a better choice than o-cresol. Perhaps one of the other terpenes with different relative reactivities toward OH and O_3 might be more suitable.

We thank the reviewer for these suggestions. We have continually turned over these ideas in the planning of these, subsequent and now ongoing experiments. In our previous study (McFiggans et al., 2019) we used CO and CH4 which both acted as OH scavengers, but also showed that their oxidation products influenced the a-pinene yield. Addition of reactive species as an OH probe cannot be guaranteed not to perturb the SOA production in the system. As mentioned in the response to referee 2, direct measurement of OH is desirable but very non-trivial. Choice of the VOCs is also nuanced. There does not appear to be a clear winner and there is always a trade-off. The fact that o-cresol does not react with ozone is useful in determination of OH-concentration from its decay in cresol-containing mixtures. An unsaturated side-chain would make this inaccessible. We are unsure about the relative merits of terpenes with differential oxidant reactivities, but have looked at such individual precursor systems previously (see Alfarra et al., 2014). These are all touched on in the discussion section.

Line 704. Suggest "...the oxidant regime is also complex."

Changed

Lines 705-6. The first part of this sentence is not clear. Why does NO_x level affect the reactivity of alkanes toward OH? Suggest rewording to make clearer.

We agree this was confusing and conflated two unrelated points. We have clarified this sentence.

Line 712. Suggest "...since anthropogenic VOCs seldom exist..."

Changed

Lines 713-4. It is asserted that reduced NO_x levels lead to reduced OH levels, but this is not necessarily true. It depends on the how high NO levels are in the first place. It could actually be the opposite that reduction in NO leads to an increase of OH. This argument needs to be reworded or removed. Also, remove the future tense in "This will inevitably lead...". Change to present tense.

Agree. Changed in both instances

Line 716-7. It is not clear what is meant by the last phrase that states that the VOCs were chosen for their reactivities which leads to their concentrations be of comparable magnitude for mixture reactivities that are comparable. First, "comparable magnitude" is a vague term that is not well defined. It is stated elsewhere that the ratios of VOCs at equivalent OH reactivity are 309:164:400, which implies the ratio of the highest to lowest amount is 2.4. Is this comparable? Second, what does comparable mixture reactivities mean? Does it mean that the sum of the VOC reactivities toward OH (1/k[VOC]) for the binary

and ternary experiments are similar to the reactivities for the single compound ones? In any case, suggest rewording the last part of this paragraph.

We have used "Comparable magnitude" loosely to imply concentration values within the same order of magnitude (here 100s of ppb). As discussed in section 2.4, the total reactivity of all systems towards the OH was roughly the same and the reactivities between the single component and the mixture experiments were similar. The sentence has been reworded for clarity.

Line 721. It is not clear what is meant by "...in the system practice." Suggest rewording.

We do not know what it means either and it is a typo that slipped through. Sentence reworded.

Line 722. This sentence has "owing" twice. Suggest rewording. Also as stated earlier, recognize that other methods of ozone measurement exist and could be used for such studies.

Agree, changed. We did try, but our alternative method for ozone measurement failed.

Line 725. It is not clear that it has been demonstrated that the amount of OH in the chamber is adequately constrained. If true, this needs to be discussed in more detail to make the case more clearly. To begin, the term "adequately constrained" needs to be defined.

As shown in Figure 6 reasonable closure of the VOC decay (within uncertainty) can be obtained arriving at OH concentration by indirect calculation. We have changed the sentence to state that some constraint on OH concentration is possible.

Line 730. The limitations due to the offline filter collection and analysis has been mentioned several times. It constrains how low initial VOC levels can be, for example. Are there alternative analytical techniques that could take the place of this approach? Elimination of this constraint would certainly make the experiments easier to design.

Online mass spectrometric techniques are approaching the mass spectral resolution enabling similar capabilities as the offline analyses with useful detection limits, though are not quite there yet. Coupling of the LToF and more recently Orbitrap mass spectrometers to Chemical Ionisation or online Extractive Electrospray show promise and it should enable easier experimental design in the coming years.

Line 727-743. It seems that employing detailed chemical models might help in the interpretation and design of the conditions and evolution of these experiments. Rather than state something "would like" be the case, specific and quantitative statements could be made. Employing such models is still possible even in the post-analysis phase of these experiments, although they could also have been very useful in the initial design of the study.

Coupled models of aerosol microphysics and photochemistry such as PyCHAM (O'Meara et al. 2021) have employed gaseous photochemical mechanisms such as the MCM and should be able to use more explicit mechanisms such as GECKO-A. These can be coupled with extensions to consider autoxidation such as PRAM (Roldin et al., 2019), but the rate constants for reasonable constraint of O_3 and OH initiated autoxidation for multiple species in complex mixtures are as yet unavailable. At the current state-of-the-science, "would likely" is the most reasonable statement possible at line 740 , since the ability of

bimolecular or unimolecular reactions to interrupt the various steps in the reaction pathways of the numerous potentially autoxidising species is dependent on too many unknown rate constants. A huge amount of activity is underway with experiments to unravel such mechanistic information in admittedly simpler systems, as yet, in a number of laboratories including our own.

Line 747. The word "straightforwardly" and elsewhere "straightforward" is used several times. Suggest rewording these sentences. Also, it is not clear how an equation can be easily applied but with consideration of oxidant regime. An equation has inputs and an output. How does this change with "consideration"? Suggest rewording.

We agree that the sentence makes too many assumptions of prior knowledge and "turns over too many pages". We have expanded with a simpler explanation.

Line 751. Suggest "...that the corrections accounting for the loss of particles...".

Changed

Line 759-60. Suggest "...since there are likely significant vapour pressure differences for the products of different chamber experiments and there are also likely dependencies of wall loss rates on species vapour pressures.

Changed

Line 750-764. This discussion is interesting and important for all chamber systems. Are there references to studies that could make this issue more quantitative? Does the EUROCHAMP consortium have information about differences in SOA yields from VOCs in chambers with differing surface-to-volume ratios and wall composition? It seems that this discussion could be more than it is "unquantifiable". Important information may exist that can be used in this study.

The referee makes an important point. There has been significant effort in the EUROCHAMP consortium to start unravelling these problems, though currently without full resolution. Once such information has been fully processed and considered, it may indeed be possible to revisit our results. The data are not complete in terms of the possible dependencies or wall materials, but should help the quantification. There are MAC data within the EUROCHAMP dataset and these are broadly in line with the other Teflon chambers. Unfortunately, there are few data across the consortium for components in the vapour pressure range of most interest and there is still significant scatter in the data that do exist. These are under active scrutiny at the moment.

Line 765. Need to define "single value yields".

This is used as opposed to full yield curves at a single value of total particle mass or VOC consumption. It is expanded in the text.

Line 768. Why is "predictions" in quotes?

Quotes removed

Line 770. Suggest "...that such predictions are valid." (use present tense) Line 771. Suggest "...the mixed yield depends on the question...".

Both changed

Line 775. Suggest "...initial isoprene concentration studied and hence...".

Changed

Line 779. Suggest changing "reference" in this context (the single VOC experiments) to something else (e.g. "base case" or "constraint"). The term "reference" could be confusing since it is used for previous related published papers.

OK, changed to "baseline comparator".

Line 780. Suggest removing the parenthesis in "...shown in Figure 5b, the..."

Changed

Line 781. Suggest coming up with a term to describe the SOA yield from α-pinene / isoprene experiments that does not include the change in isoprene concentration, since the normal approach to calculated yield is the ratio of the increase in SOA divided by the decrease in VOC. Developing terminology for this case is preferable to stating "excluding isoprene in the calculations". One could imagine using Y (for yield) with various superscripts or subscripts to indicate the various cases, for example $Y^{pin,isop}$ and $Y^{pin,isop}$ could (1) indicate the SOA yield from a $_{pin,isop}$ pin binary α-pinene / isoprene system (superscript) using the loss of both compounds in the calculation (subscript), while (2) could indicate the SOA yield from a binary α-pinene / isoprene system (superscript) using the loss of α-pinene only in the calculation. Just a thought.

This is interesting and in direct opposition to the contention of referee 1 who states that it is unimportant whether consumption of a VOC in a mixture is included or not if it doesn't contribute particle mass. We have adopted a similar formalism to that suggested in the revised manuscript to reflect these cases.

Line 813. The question of whether the inorganic aerosol mass should be somehow included in the yield is important. Has anyone done multiple experiments (say with α-pinene) under identical conditions with varying amounts and identities of inorganic seeds, perhaps also including different size distributions? This seems to be a critical part of performing such experiments in the laboratory chambers. If such work exists, suggest referring to it here and adjusting the discussion accordingly.

We are not aware of such experiments. It is not completely straightforward to capture all possible dependencies and there are measurement considerations for different components, but it should be possible.

Lines 819-20. Suggest "...composition is an important topic for a future study." Line 823. Suggest "...chemical composition would provide important...".

Both changed

Line 835. It Is not clear what is meant by the phrase "from the beginning of the experiment". Suggest removing it.

Clarified.

Line 840. In the discussion of which process could form the substances that are observed on the filters collected in ternary experiments, it should also be mentioned that there are known processes of oxidation of surface aerosol substances by gas-phase oxidants, and also condensed-phase chemical oxidation. Addition of one or more references here would be helpful to the reader.

Such processes have indeed been recognised for some time and we now refer the reader to Liu et al. (2014) and Turpin et al. (1994)

Line 843. Should the term "ternary" be added to "...only found in the ternary mixed system."?

No, they are found in a number of mixtures; the sentence has been revised for clarity.

Line 846. Remove right parenthesis on "Figure 10a".

These are now in the SI and referred to accordingly

Line 849. Suggest "...there are confounding differences..."

Changed

Lines 851-2. Are there composition data from the FIGAERO-CIMS during the experiments (not just at the end)? If so, consider a way to present these data, too.

The data shown are from FIGAERO-CIMS and panel b shows the different time-series behaviours of $C_7H_7NO_4$ between experiments. The measurements presented here are indicative and full time-resolved measurements of the FIGAERO-CIMS are presented in companion papers (Shao et al., 2022b, Du et al., 2022 and Du et al., 2022, in prep).

Line 861. Suggest "...which expresses the FIGAERO-CIMS...".

Changed

Line 862. Suggest "...in the mixture and in the single...".

Changed

Line 885. This reviewer does not think the word "certainly" is appropriate here. It is conceivable, possible, and even highly likely that scavengers could influence the oxidation product distribution, but it is not certain until the appropriate experiment has been performed. Suggest rewording.

Agree that this has yet to be proven, so changed

Line 886. Suggest "...secondary oxidant formation occurs in the real...". While this is a true statement, it does not necessarily justify that initial mixed VOC experiments must be conducted in mixed oxidant environments. It is better to conduct the mixed VOC experiments with single oxidants first and then graduate to mixed oxidant situations.

We would contend that this depends on the objectives of the experiment. A phenomenological demonstration of the importance of full complexity vs individual oxidant system is completely possible. We agree that resolution of a specific oxidation process requires the approach stated. There is value in both approaches and inability to conduct an "ideal" experiment should not preclude collection of useful information from less "clean" systems.

Line 888. It is not true that high peroxide concentrations are required in experiments that use peroxide as an OH precursor. The peroxide can be added constantly to maintain a relatively low steady-state level. This is actually preferred because OH reacts rapidly with hydrogen peroxide. Suggest rewording.

Thanks for the advice. Reworded.

Line 892. Suggest "...may increase the OH : O_3 ratio such that the OH reaction pathways dominate...".

Changed

Line 897. The statement "...maybe more suited to targeted laboratory studies than to chamber experiments" is confusing since chamber studies are target laboratory studies. Suggest different wording for "targeted laboratory studies" such as "flow tube kinetic studies" or something similar.

Point taken. Reworded.

Line 904. This sentence is confusing because it uses "resolution" and "temporally resolved" together. One needs to be clear whether resolution refers to temporal or mass resolution (as in mass spectrometry). Suggest rewording.

Again – sloppy language. Changed

Line 906. Suggest "...reactor experiments to study multiple steady states...". The authors should also consider more detail in what is meant by multiple steady states, along with references.

We were referring to the sorts of studies conducted in McFiggans et al. (2019). Changed

Line 909. Suggest "...thought it should be recognized that oxidation and SOA formation occur during...".

Changed

Line 910. It is not clear what is meant by "mixed night-time oxidation by NO_3". Also, suggest "...should be considered" instead of "should not be forgotten."

We should have stated "in mixtures" rather than "mixed". Changed.

Line 915. Suggest "…to their interpretation, several important observations…"

Changed

Line 917. It is not clear what is meant by "photochemical trajectory". Suggest defining somewhere with discussion to amplify its importance in the present study.

OK, this is referenced back to Figures 1 and S1 and expanded.

Line 925. Suggest "…existence and to quantify any interactions affecting the observed SOA mass and yield."

Changed

Lines 928-9. Here is "straightforward" used in two sentences in a row. Suggest rewording.

Reworded

Line 931. This reviewer is not sure the term "reference point" is the best. Suggest rewording.

Changed to "baseline comparator"

Line 939. See earlier comment about "unique-to-mixture".

"Uniquely found in the mixture" is now used in the revised caption of the figure, now found in the SI.

Line 940. Suggest "…of the particles depends on the rates…".

Changed

Line 942. Suggest "…for our understanding of atmospheric…".

Changed

Line 943. Suggest "…the interpretation is complex, and both the experimental design and evaluation need to be…".

Changed

Figure S4 caption. Suggest "…in the single precursor α-pinene and…". Also, why is the x-axis scale of the plot logarithmic? The symbols are very similar and hard to distinguish. Suggest changing to make clearer.

We have changed as well as enlarged the size of the symbols in the updated Figure S4 (see below) to improve it's clarity. The x- axis is logarithmic to enable the low mass points to be distinguished which is not possible on a linear scale.
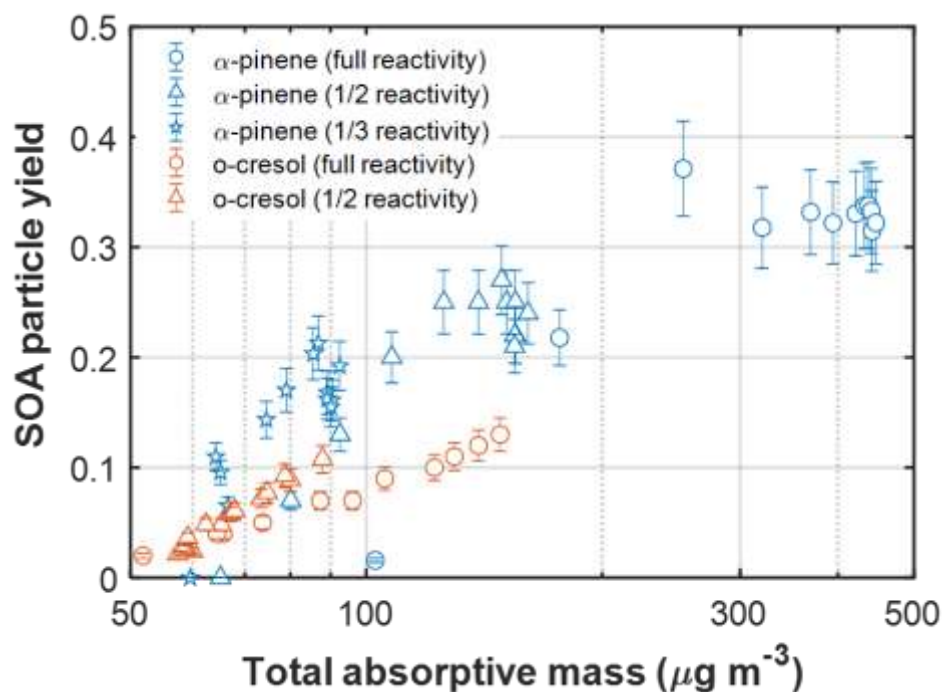
Figure S4: SOA particle mass yield as a function of total absorptive mass, including the remaining inorganic seed mass, in the single precursor α-pinene and o-cresol experiments at all initial concentrations. Error bars represent the propagated uncertainties in all measurements and in the particle wall loss corrections applied.

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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 3 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):

Voliotis et al. describe a comprehensive set of chamber experiments of the secondary organic aerosol (SOA) formation from individual VOCs as well as VOC mixtures including both biogenic VOCs (isoprene and α-pinene) and anthropogenic VOC (o-cresol). By novel experimental design of VOCs with comparable reactivity, it nicely compared the SOA form signal precursors with that from their binary and ternary mixtures, revealed very interesting results, as well as the complexity in the experimental design and evaluation. It provides valuable information and discussion for our understanding of chamber studies of VOC mixture systems, and also guidance and inspiration for future study of such essential topic. I would recommend the publication of this solid and excellent work. However, there are a few comments I would like the authors to address.

General comments

This paper is very long. I suggest restructuring and shortening it. I understand that there are too many things that have to be considered and also worth to be mentioned in experimental design and evaluation. However, I suggest focusing on what you did rather than what you did/could not do (and the reason behind), clearly separating method, results, and discussion, and helping readers to quickly get the most important results and information from the paper.

We thank the referee for their suggestion and agree that the organisation could benefit from attention. We have substantially changed the paper in response to all referees. We have concentrated on the core messages of experimental design, implementation, results and interpretation and have moved all the results from the companion papers along with the associated Figures, into the supplementary information. These are now only referred to in the discussion section along with some discussion of the expansion of the interpretations in each paper. This is because of the progress made in the reviews and publication of the companion papers and the requirement to maintain the focus on the key new points in the current paper.

I appreciate that this paper also offers the chemical or physical properties measured by both online and offline instruments, which could be used to explain the interactions found in VOC mixtures experiments. However, I was a little bit disappointed to see some very general introduction/results, but not a close link to the most interesting findings, e.g. shown in Fig. 5. Figures like Fig. 13, in my opinion, are not necessary to put there and make the paper too long. It could be mentioned e.g. in the discussion.

Figures 7-13 of the original manuscript have been moved to the SI, along with their description. They are now only referred in the discussion. This has led to much shorter and concise revised version.

Specific comments

Line 26 to 28: It is difficult to get "½ initial reactivity" in the abstract. Please add more explanation.

We already state "Comparing experiments conducted in single precursor systems at various initial reactivity levels (referenced to a nominal base case VOC reactivity)…" in the previous sentence. We have expanded the parenthesised text to state "referenced to a nominal base case VOC reactivity, e.g. halving the initial concentration for a ½ initial reactivity experiment"

Line 30: If it is too small, could you say "a suppression of the SOA yield from o-cresol is not found when it is mixed similarly with isoprene"?

Changed to "no suppression or enhancement of the SOA particle yield from *o*-cresol was found when it is mixed similarly with isoprene"

Line 43: The reference could be updated.

Updated

Line 224: It was already mentioned in line 196.

Repetition deleted, but "non-acidic" added at first mention.

Line 338: Missing references for FIGAERO-CIMS and Orbitrap.

We have not referenced established commercial instruments in the table (only custom-built techniques or instruments), but refer to our companion papers where they are used and comprehensively discussed, inline in the text.

Line 390: Please specify the terms involved in the equation.

Terms defined

Line 404, Figure 2:the resolution of the figure is low (the same as most other figures).

The resolution of the figures have been updated throughout.

Line 404: b) is o-cresol and c) is isoprene.

This has been corrected in the revised version of the figure

The description of colors leads to confusion and it is enough with the legend.

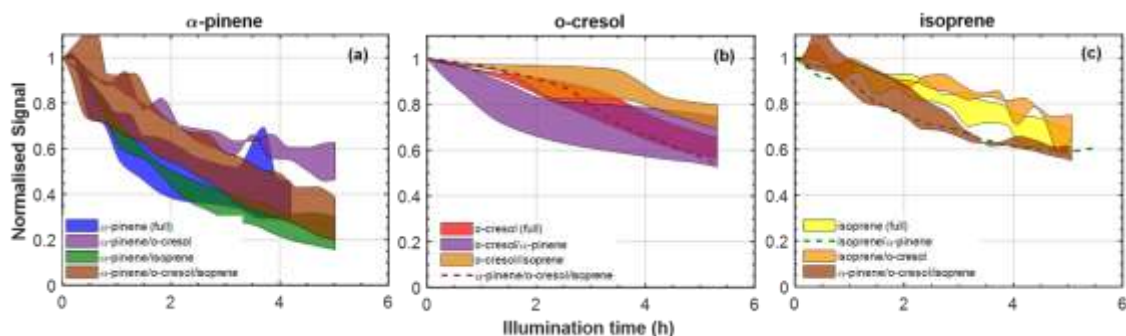
Colour description removed from the revised caption:

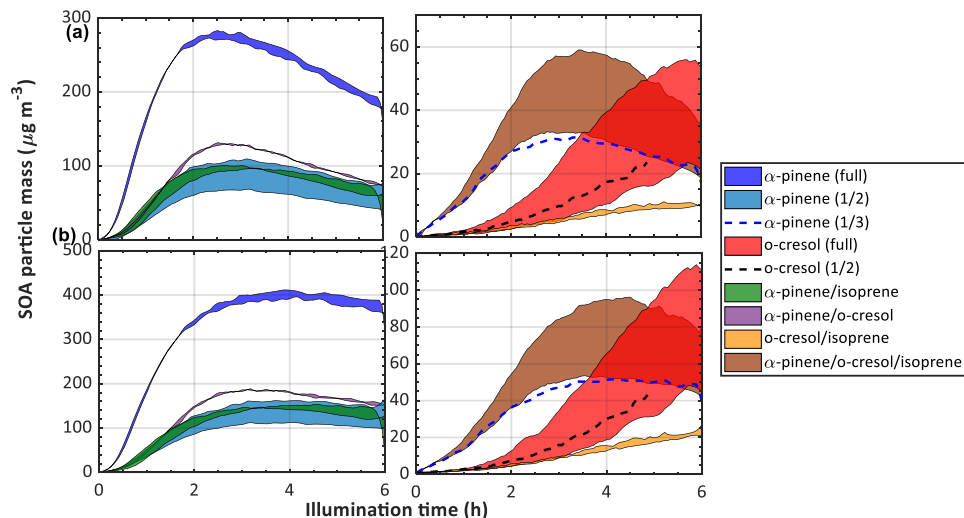
"Figure 2: Decay rates of each VOC across all mixtures; a) α-pinene, b) o-cresol and c) isoprene. The shaded areas represent 1 standard deviation around the solid line mean value of all experiments."

Why in (b) the line of ternary experiments doesn't have shaded areas?

Instrument failures on the repeat experiments led to the lack of measurements of the *o*-cresol decay. Therefore in this system, *o*-cresol decay is shown for 1 experiment only.

It is not clear, that whether the decay rate of signal VOC comes from all full reactivity, half reactivity, etc. or only one experiment.

All the decay rates are given at the same initial reactivity level. Therefore, for the single precursor experiments at full reactivity, for the binary systems at ½ reactivity and for the ternary system at 1/3 reactivity. The legends of the figure have been revised to clarify this. The revised version of the figure is shown below:

Line 429, Figure 3: Honestly, it is a very interesting figure, but difficult to read.

This has been revised according to the comments of other reviewers, separating the panels for clarity:

Line 456-457: Need reference.

We now refer back to the original Bowman et al. (1997) paper for this

Each curve comprises multiple data points measured over the duration of each experiment. The caption of the figure has been revised (also in accordance to a similar comment from reviewer #1) to:

"Figure 4: SOA particle mass yield as a function of mass formed in the single precursor α-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."

All terms defined: Δ_{VOC} in each case is the consumed concentration of parent VOC and the Δ_m represents the formed SOA particle mass from each parent VOC. The equation has been re-expressed as follows:

$$Yield_{pred.} = \frac{\Delta m_{VOC1} + \Delta m_{VOC2} + \Delta m_{VOC3}}{\Delta VOC1 + \Delta VOC2 + \Delta VOC3}$$

The total signal of identified peaks in the range of m/z 200-550 (excluded the reagent ions, I_2^-: m/z 253.809492 and I_3^-: m/z 380.713964) was used to normalise the ion signal'. The details in the data processing of FIGAERO-CIMS were described in Voliotis et.al (2021) and Du et.al (2022). Figure 8 is now in the SI and the results are described in the extended caption, with discussion in the main text.

The figure aims to illustrate the capability of FIGAERO-CIMS to observe the chemical compositions at different experimental stages by comparing mass spectra at 0.5 hours and 5.5 hours. In order to make this comparison clearer, the y scale was set the same at the same time point. Truncating the highest peaks allows easier comparison of the spectra.
The caption of Figure 8 (now moved to the SI) now reads "Mass spectra were taken in the single precursor α-pinene (a1 and a2), o-cresol (b1 and b2) and mixed α-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 start of illumination of the MAC.'

Our original paper fell into the trap of introducing all the techniques and presenting some data but not discussing in much depth. We have made clear that the results presented in Figures 7 to 13 are not the key focus of this paper, by moving them into the Supplementary Information. These results and their considerable expansion are reported in the companion papers but discussed in brief here. We agree that the number of compounds detected in each mode, how they can be classified and their relative

proportions of the signals, as well as the possible methodologies for optimal combination of the different techniques will all be of considerable interest and full details and discussions are presented in Shao et al. (2022a,b) and Du et al. (2022a,b)

Line 600: It is not clear what is "in -ve ionisation mode 57% of the signal in 48 individual peaks with nC > 10 and in +ve mode 60% in 115".

Rephrased to " Clearly a substantial fraction of the signal in compounds uniquely found in the mixture is found at carbon number greater than any precursor VOC. 57% of the signal with nC>10 was found in 48 compounds uniquely found in the mixture in negative ionization mode, and 60% of the signal with nC>10 in 115 such compounds in positive ionization mode."

Line 614: It is again not clear how the normalization was performed.

The total signal of identified peaks in the range of m/z 200-550 (excluding the reagent ions, I_2^- at m/z 253.809492 and I_3^- at m/z 380.713964) was used to normalise the ion signal. The details in the data processing of FIGAERO-CIMS were described in Voliotis et.al (2021) and Du et.al (2022).

Line 636: The method of the calculation of C should be mentioned earlier.*

We agree with that additional information is needed. We have moved Figures 7 to 13 to the SI and an extended caption to Fig. S11 describes the procedure for calculating the C*:

"The C* was calculated using the gas to particle ratio of each ion and absorptive partitioning calculations. The FIGAERO-CIMS signals in both gas and particle phases were converted into concentrations (ions m^{-3}) based on the signal strength and the volume of air sampled. Using the fraction of each species in the particle phase and the total absorptive mass (in this case the total concentration of organic compounds), the saturation concentration of each identified product was calculated (see Donahue et al., 2006)"

Line 842: Please mark Shao et al. in prep.

Done

Line 846: The contributions of different isomers are not very different. I doubt whether it could be used to explain the different time trends measured by FIGAERO-CIMS.

Indeed the LC-Orbitrap MS determined contribution of each isomer is not sufficiently different to explain the different time trend from the FIGAERO-CIMS measurements. Panels a and b of Figure 10 provide complementary information but do not explain each other. To unravel the temporal behaviour of the FIGAERO time series, we employed hierarchical clustering analysis , investigating the different behaviours of the same compounds in different systems (Du et al., in prep). These differences will be attributable to a range of additional factors to the variable isomer concentration such as variable oxidants, VOC: NOx ratio etc. This is all recognised in the amended text and we have made it clear that there is no simple relationship linking the behaviour shown in Figure 10a and b.

Line 852: Similarly, please mark it Du et al. in prep.

Du et al. (2022) is ACP accepted and Du et al. (2022b) is in prep – marked.

Line 876: Wang et al.?

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