

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:

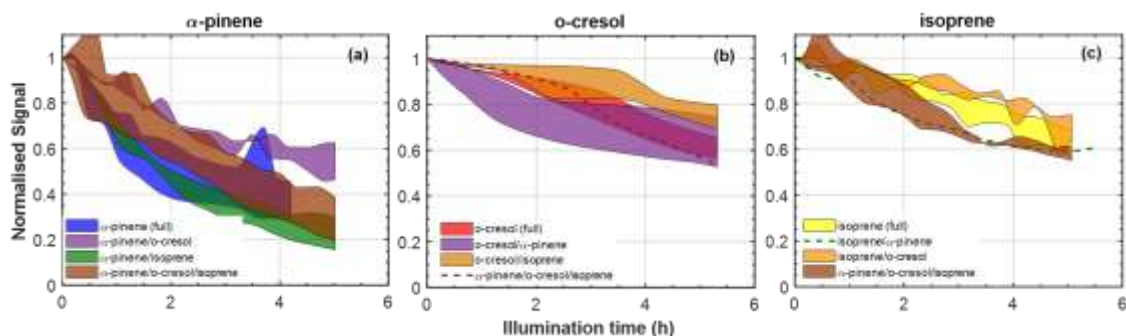
“Figure 2: Decay rates of each VOC across all mixtures; a) α -pinene, b) o-cresol and c) isoprene. The shaded areas represent 1 standard deviation around the solid line mean value of all experiments.”

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.

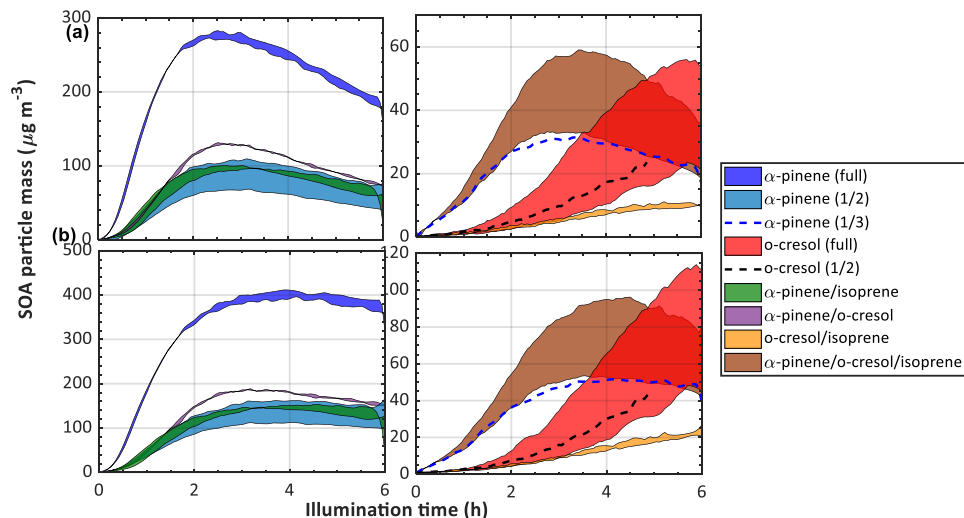
It is not clear, that whether the decay rate of signal VOC comes from all full reactivity, half reactivity, etc. or only one experiment.

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 1/2 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

Line 461, Figure 4: it is not clear how these data points were calculated

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.”

Line 489: Please specify the terms in equation 4.

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:

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

Line 580: It is not clear how the normalization was performed. As I- signal should be very high, the normalized signal could not as high as 0.01 or even 0.1.

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.

Line 586, Figure 8: It is better not to cut the highest signal. Also, please mention the mass spectra were from which experiments.

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.’

Line 591 – 598: As both the FIGAERO-CIM and the LC-Orbitrap were used for particle-phase chemical composition, a general comparison or information of how many compounds were detected/identified for both will be interesting, and how to combine the molecules detected in positive and negative modes with the LC-Orbitrap.

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.?

References included

References

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