

## General Comments:

This work by Shao et al. is a follow up to the work by McFiggans et al. in Nature 2019 on the impacts of mixed VOC systems on SOA formation. They performed a series of batch mode chamber experiments with single and mixed precursors of biogenic and anthropogenic origin in the presence of NO<sub>x</sub> and aerosol seed. Offline analysis of the SOA composition was performed primarily with LC-MS to elucidate which species dominate and dictate the SOA formation in mixtures and identify any cross products. This work is novel and of value to the community, although I find it to be overly verbose and rambling and suggest editing to make it more concise and flow better if possible. This is appropriate for ACP after addressing the other suggestions below.

## Specific Comments:

Line 134: I think this is well established and suggest re-wording “might be the reason” to something more definitive

Line 134 revised from “which *might be the reason*” to “*which is the reason...*”.

Line 207: What is the residence time in the chamber?

The MAC is operated as a batch reactor and is not operated in “flow through” mode. The air is held continuously after introduction, as described in Shao et al. (2022), so essentially has an infinite residence time (though component lifetimes clearly would be limited by the losses to, and interactions with, the Teflon walls). The experimental duration is typically 6 hours, though experiments up to 24 hours are possible.

Section 2.4.1: Is it possible for chemical transformations to occur during the 2 hr ambient temperature rest, sonication, or drying? Would this be observable? Can you comment on how this may impact results?

It is difficult to determine the quality of the aerosol extraction procedure using non-targeted analysis due to the difficulty of unknown compound identification. The analytical standards for SOA products are limited and only a few molecules out of the thousands detected compounds might be known. Therefore, it is also difficult to determine sample extraction recoveries during sample extraction procedures, since various compounds will have different recovery efficiencies that can be influenced by the molecular structure (Priego-Capote and Luque De Castro, 2004). However, we note that the sample extraction procedure performed in this study is common practice for the analysis of OA, with the majority of studies using either water or methanol as the extraction solvent, followed by sonication and evaporation (Gao et al., 2006; Hamilton et al., 2008; Kourtchev et al., 2016). It should be noted that we used methanol as extraction solvent since sonication using water can result in the formation of hydroxyl radicals (Miljevic et al., 2014). Moreover, a procedure-controlled sample using a blank filter subject to the same extraction procedure, was performed and analysed using LC-Orbitrap MS analysis. Any artefacts introduced into the samples during sample preparation were excluded from the sample data (see Pereira et. a. 2022 for further information).. However, This does not provide insights into potential chemical transformations in the OA samples. Investigating

potential chemical transformations during the preparation of the OA samples using non-targeted screening would be incredibly challenging. A control sample (*i.e.* a portion of the same OA sample to allow comparison) would still need to undergo some form of extraction into solvent to allow LC-MS analysis. Further, evaporation and resuspension of the sample into a smaller volume (*i.e.* sample concentration) will almost certainly be required to allow detection of the trace-level compounds present in OA. However, individual compounds within OA could be targeted to investigate possible chemical transformations, spiking a known quantity of a chemically labelled authentic standard (*e.g.* deuterated) into the OA sample before solvent extraction. This would allow any chemical transformations to be observed and the extraction recovery of the spiked compound to be determined. We recommend in Pereira *et. al.* 2022 investigating the recovery efficiencies of authentically identified compounds in future work to quantify any potential losses and provide insights into the quality of the extraction procedure. The work presented here was performed prior to the publication of Pereira *et. al.* 2022 and subsequently does not include this in investigation.

Line 304: Where would the sodium and potassium come from?

Sodium and potassium could come from several sources during sampling preparation and analysis, such as the mobile phase additives, solvent impurities and so on. The main source is leaching from glassware used to prepare the solvents (Kruve and Kaupmees, 2017). The sentence in the line 302- 304 rephrased to

*“The method provides molecular formulae assignment of detected compounds using the following elemental restrictions: unlimited carbon, hydrogen and oxygen atoms, up to 5 nitrogen and sulphur atoms, and in positive ionisation mode, 2 sodium and 1 potassium atom are also allowed (sodium and potassium are typically introduced into the samples via glassware).”*

Figure 2: Are these common molecular *structures* or molecular *composition*?

These are common discrete molecules. We compared the molecule list between different precursor systems and identified the common molecules which were only considered to be the same detected molecular species if they had a retention time within 0.1 minutes.

The captions in Figure 2 rephased to “ *Number of common discrete molecules and unique compounds in single and binary precursors mixed experiments detected by negative ionization mode LC-Orbitrap MS. Product are considered identical in the mixed and single precursor systems if the molecules has the same empirical formula and a retention time difference <0.1min.*”

Also, the caption in Figure 3 rephased to “*Number of common discrete molecules and unique compounds in single and binary precursors mixed experiments detected by positive ionization mode LC-Orbitrap MS. Product are considered identical in the mixed and single precursor systems if the molecules has the same empirical formula and a retention time difference <0.1min.*”

Figure 4: Why does essentially all the signal contain nitrogen for cresol and any mixtures with cresol? This is discussed ~line 520 but not the reasoning for why N-containing species are highly dominant.

Nitrogen containing compounds, such as those containing amide groups or nitro groups, efficiently ionize using electrospray ionization (Oss et al., 2010). As the MCM v3.3.1 and our study shown, *o*-cresol photo oxidation produces a number of different kinds of nitro-aromatic compounds, such as methyl-nitrocatechol and methyl-nitrophenol. These compounds have high negative mode sensitivity using electrospray ionisation, contributing to substantial signal in the systems that contain *o*-cresol.

This is mentioned in line 526-528, line 576-577, line 783-784, line 851-852, and line 954-956 in the manuscript. Reference ( <https://doi.org/10.1021/ac902856t> ) will add in line 528 to further support the explanation.

Line 467: Suggest using HOM definition from Bianchi et al ( <https://pubs.acs.org/doi/10.1021/acs.chemrev.8b00395> ): highly oxygenated organic molecules

The definition of HOM in line 467 had been rephased to “highly oxygenated organic molecules”

Lines 466-472: This section on HOM is not well fleshed out and doesn't seem to flow with the discussion. Suggest removing or re-writing. Please add a reference for this sentence, or remove: “Autoxidation may therefore contribute to CHO products with carbon numbers 16 – 20 in  $\alpha$ -pinene oxidation”

We rephased the sentences from line 466 to 472 as shown below:

*“Autoxidation of RO<sub>2</sub> radicals in the gas-phase occurs rapidly via inter/intramolecular hydrogen abstraction leading to forming R radicals with subsequent O<sub>2</sub> addition (Mentel et al., 2015; Jokinen et al., 2014). The new RO<sub>2</sub> radicals can undergo further autoxidation reaction, or react with RO<sub>2</sub> to generate dimer accretion products (Zhao et al., 2018; Berndt et al., 2018), leading to so-called highly oxygenated organic molecules (HOM) with very-low volatilities (Bianchi et al., 2019). Autoxidation may therefore contribute to CHO products with carbon numbers 16 – 20 in  $\alpha$ -pinene oxidation (Berndt, 2021; Ehn et al., 2014)”*

Line 477: Please state how much SOA was formed. It is confusing that this line (and above) states ~0  $\mu\text{g}/\text{m}^3$  was formed but the section goes on to discuss the compounds measured in the particle phase

The SOA particle mass was 0.1  $\mu\text{g}/\text{m}^3$  in single precursor isoprene system. The sentence in line 477 rephased to “As also seen in Fig.1(a), negligible SOA particle mass was generated in the single precursor isoprene system (0.1  $\mu\text{g}/\text{m}^3$ , close to our chamber background”. We measured the SOA particle mass by using the online HR-TOF-AMS, which detected negligible mass in the chamber, at the same order as the background chamber levels. This does not mean that there were no particulate components derived from isoprene present, just that the total mass was practically indistinguishable from the background mass using our online instrumentation. The compound measurements we report were obtained from offline LC-orbitrap MS analysis, with its ability to detect compounds with trace sensitivity much lower than the limit of detection of the AMS. The compounds could be detected by LC-Orbitrap MS, and use automate non –

targeted screening method to assign the molecular formulae as long as the masses error < 3 ppm, signal-to-noise ratio > 3, and the isotopic intensity tolerance was within  $\pm 30\%$  of the measured and theoretical isotopic abundance.

Lines 493-494: This doesn't reflect the current state of knowledge and is an insufficient explanation/discussion. Several recent studies have shown that small particles are detected in SOA as a result of decomposition, typically via thermal processes, during analysis. While this work doesn't utilize heating techniques, it does involve substantial sample prep (see comment on section 2.4.1).

As stated in the response for the comment on section 2.4.1, it is difficult to determine the likelihood of potential chemical transformation in the OA sample during the aerosol extraction procedure. An extra sentence will be added at line 495:

*“The possibility that small detected molecules were formed in the filter sample extraction process cannot be ruled out. For example, degradation of organic compounds can be induced by ultrasonic extraction of particulate matter from filters (Miljevic et al., 2014; Mutzel et al., 2013),”*

Lines 496-498: I'm confused why the experiment would be designed in a way that is well documented to not make SOA when the stated point of this work is to make SOA and measure the particle phase composition? Please explain the reasoning for this experimental design and how this advances our understanding of multi-component SOA formation.

Our experimental program aims to establish a framework to understand interactions in systems of mixed anthropogenic and biogenic VOCs. Therefore, we choose precursors considering the potential diversity in VOC sources contributing to the ambient atmosphere, building on the previous insight from McFiggans et al.(2019) which used a binary mixture of biogenic low yield (isoprene) and high yield ( $\alpha$ -pinene) precursors. The aim is to further investigate the interaction in systems of mixed low, moderate or high yield VOCs, with both anthropogenic or biogenic species able to compete for the available OH.

There is a clear indication of suppression of the yield of  $\alpha$ -pinene in its mixture with isoprene, but as with the *o*-cresol / isoprene mixture, there is a possible indication of enhancement, though this is too small to be unambiguous. In the ternary system, it is unclear if there is a suppression or enhancement effect with regard to measured total SOA particle mass, but chemical interactions are evident from the unique-to mixture components. All these results about SOA yield across different precursors systems, details of experimental design, and the complexity of the systems introduced substantial challenges to their interpretation were comprehensively elucidated in the companion paper Voliotis et al. (2022).

We still could measure and analyse the SOA particulate product from isoprene, which is well documented to make little SOA particle mass under neutral seed conditions, by use of the LC-Orbitrap MS technique and its unprecedented high-resolution accurate mass (HRAM) allowing unambiguous identification of molecular formulae. .

Line 501: Can you be sure these species are created from isoprene + OH and not impurities in your isoprene source or chamber contamination?

The isoprene gas precursor was introduced into the chamber by injecting liquid isoprene (Sigma-Aldrich, purity  $\geq 99\%$ ) through a rubber seal into a glass bulb that temperature was kept at approximately  $100^{\circ}\text{C}$ , and flush to the chamber by using nitrogen as carrier gas. The glass bulb was warm and flushed with  $\text{N}_2$  during the “pre-experiment” protocol before the conducted experiment ensuring contamination in the glass bulb was flushed out and maintain cleanness. Thus, we are confident that these species are not contamination or impurities in the isoprene source.

Our chamber had conducted off-gasing and actinometry experiments regularly to determine the chamber background contamination. Filter samples also been collected after each off-gasing and actinometry experiment, that followed the same sample extraction procedure and LC-Orbitrap MS analysed method. None of the reported compounds were found in these background experiments and any contamination from chamber introduced into the experimental samples can therefore be excluded.

Line 679: Here you mention the possibility of fragmentation of larger species resulting in the smaller species measured in the particle phase. Please include references (e.g. <https://pubs.acs.org/doi/abs/10.1021/acs.est.5b04769>).

The reference (Lopez-Hilfiker et al., 2016) will be added into the text of manuscript.

Line 765: It isn't clear to me that accretion reactions have occurred during SOA formation rather than alterations during sample prep and analysis. Additionally, if they did occur during the experiment, can you be sure that accretion products would still form under atmospherically relevant precursor and SOA concentrations?

The intensity weighted average values of nC clearly show accretion products to be present in the single precursor isoprene system, the binary  $\alpha$ -pinene-containing systems and the ternary system in positive ionization mode. It is indeed difficult to guarantee that the OA chemical transformation did not happen during sample preparation. Therefore, the sentence in line 765 has been rephrased to

*“It is apparent in the positive mode that accretion reactions occurred, and its products play an essential role in the single precursor isoprene system, the binary  $\alpha$ -pinene-containing systems and the ternary system. It cannot be discounted that chemical transformation may occur during filter sample preparation, which might impact on the intensity weighted average values of various chemical properties.”*

Some of the accretion products, such as  $\text{C}_{21}\text{H}_{33}\text{NO}_4$  in binary  $\alpha$ -pinene/*o*-cresol system,  $\text{C}_9\text{H}_{11}\text{NO}$ , and  $\text{C}_8\text{H}_8\text{O}_{10}$  in binary isoprene/*o*-cresol system were found uniquely in the mixed precursors system with non-negligible normalized signal abundance, enabling their use as tracers in the ambient environment.

### **Technical:**

Throughout manuscript:  $\text{NO}_x$  should have a subscript “x” and be  $\text{NO}_x$

Changed

Throughout manuscript: change instances of “ml” to “mL”

Changed

Throughout manuscript: change instances of “ug” to “µg”

Changed

Line 222: particles counter à particle counter (plural to singular)

Changed

Reference:

Berndt, T.: Peroxy Radical Processes and Product Formation in the OH Radical-Initiated Oxidation of  $\alpha$ -Pinene for Near-Atmospheric Conditions, *The Journal of Physical Chemistry A*, 125, 9151-9160, 10.1021/acs.jpca.1c05576, 2021.

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