This study determined the photooxidation of single and mixed biogenic (isoprene and α-pinene) and anthropogenic (o-cresol) precursors in the presence of NOx and seed particles. It is interesting to determine the chemical interactions in mixed VOC systems by using non-targeted LC-Orbitrap MS. This work is novel and provides some interesting data, but the methodology and discussion can be described in detail. There are still some comments need to be addressed:

1) Line 211-213: Isoprene is the most abundant biogenic VOC emission and α-pinene is one of the most abundant and widely studied biogenic monoterpene. There are lots of anthropogenic VOC precursors, e.g., BTEX, which are the most abundant aromatic VOCs. But why o-cresol was chosen as an anthropogenic precursor was not described in this and previous studies (Voliotis et al, 2022).

The primary reason for selection of *o*-cresol was its comparable reactivity toward the OH radicalwith those of isoprene and α-pinene, allowing *o*-cresol to have initial isoreactivity at concentrations comparable to the other precursors so that the oxidation products from each precursor are likely to be of comparable abundance in a mixed VOC system. Other anthropogenic VOC precursors such as benzene, ethylbenzene, o-xylene, p-xylene, m-xylene, and toluene ("BTEX"), whilst more abundant in the ambient atmosphere, have a significantly lower rate coefficient toward OH than the two biogenic VOCs as shown in the table below (Atkinson, 2004; Calvert, 2002). This would require substantially higher concentrations of each, compromising our experimental design.

VOC	Rate coefficient at 298K (k/cm^3 molecule^{-1} s^{-1})
Benzene	1.2×10^{-12}
Ethylbenzene	7.0×10^{-12}
o-xylene	1.36×10^{-11}
p-xylene	1.43×10^{-11}
m-xylene	2.31×10^{-11}
toluene	5.60×10^{-12}
o-cresol	4.10×10^{-11}
α-pinene	5.30×10^{-11}
isoprene	1×10^{-10}

This choice does not devalue the study. *o*-cresol is an anthropogenic VOC with a moderate SOA yield that is directly emitted to the ambient environment during coal, wood, and municipal solid waste combustion and is an oxidation product of toluene (e.g. from automobile exhaust), which is among the most abundant anthropogenic hydrocarbons in the atmosphere (Deng et al., 2017; Zhao et al., 2004)

This information has been added in lines 211-213: "*Ortho-cresol (o-cresol) was chosen as an anthropogenic precursor with a moderate SOA yield, between that of isoprene and α-pinene. o-cresol has reactivity toward the hydroxyl radical (OH) that is comparable to those of the chosen biogenic VOCs (Atkinson, 2004) and a negligible reactivity towards ozone. Hence, the oxidation products from each precursor are likely to be of comparable abundance in a mixed systems.*"

2) Line 284-286: As no denuder was used to remove VOCs and oxidants, particle collected on filters will/may perform further oxidation (or reaction). Would this be observable in this study? How to prove that no further reactions have been performed on the filter? Can you comment on how this may impact results?

We thank the reviewer for pointing this out. Filter sampling can exhibit both negative and positive artefacts. Gas-phase organic compounds can be adsorbed on the filter medium and on particle mass collected during sampling, whilst volatilisation of "non-involatile" particulate components can reduce the collected mass. Adsorption leads to the overestimation of organic particle mass, while volatilisation results in its underestimation. It is difficult to isolate and quantify these two artefacts since they can occur simultaneously (Subramanian et al., 2004). Additionally, organic particulate products may be formed by further reaction on the filter (Cheng et al., 2009), changing the chemical composition of collected particulate matter.

Our samples were rapidly collected (emptying the chamber through the filter in 5 or 6 minutes) and it is not possible to effectively denude the gases at the flow rate through the filter in our chamber. Whilst this leads to limited time for adsorption and reaction, it is difficult to quantify these impacts. It should be noted that the formation of products from such reactions could also occur as a result of gas-particle collisions during the experiment during the much longer residence time in the chamber. A companion paper in this project characterising the chemical composition using online (FIGAREO-CIMS) and offline mass spectrometric (LC-Orbitrap MS) techniques showed high consistency between the online I^--CIMS and offline negative ionization mode (Du et al., 2021) within the limitations of the techniques. Whilst both techniques use filter collection, this is indicative that the further reactions on the filter after collection do not substantially influence the overall composition, and reactions during collection at very different flowrates and sampling times are comparable (or negligible). Further work is required to fully quantify any such artefacts.

A short discussion to this end has been added in line 294 in manuscript: " It is noted that *both positive (conversion of gas phase organics to particulate form) and negative (volatilisation of particulate organic compounds) artefacts are possible during collection of particulate matter during filter sampling, resulting in overestimation and underestimation of particulate organic carbon, respectively. The samples were rapidly collected in our experiments (emptying the chamber through the filter in 5 or 6 minutes), precluding the ability to effectively denude gases at the flow rate. Whilst gases may be adsorbed / adsorbed on the filters, it is challenging to quantify these impacts. Formation of products of reactions in the particles themselves could also occur after to gas-particle collisions during the experiment with a much longer residence time in the chamber.*

Du et al. (2021) combined the online (FIGAREO-CIMS) and offline mass spectrometric (LC-Orbitrap MS) techniques to characterise the chemical composition in the same systems. It was reported that the distribution of particle-phase products is highly consistent between the I^--CIMS and LC-Orbitrap MS negative ionisation mode for the α-pinene SOA products, suggesting near negligible (or at least comparable) gas phase absorption artefacts introduced during filter collection in both techniques."

3) Line 298-304: Any recovery test has been performed? If yes, please provide more information about the extraction recoveries.

No recovery test was performed in this study.

This information will be added in the line 324: "*The efficiency of the aerosol extraction procedure using non-targeted analysis in this study is difficult to determine owing to the limitation of unknown compound identification. Few molecules of the thousands detected can be identified in the analytical standards for SOA products. It is also difficult to determine sample extraction recoveries since compounds have different recovery efficiencies determined by their molecular structure (Priego-Capote and Luque De Castro, 2004). Much further work on the recovery efficiency is required to quantify potential losses and provide insights into the quality of the extraction procedure.*"

4) Line 360-361: "The SOA particle mass continued to increase at the end of the experiment in the single VOC o-cresol and binary isoprene/o-cresol systems". Have the authors tried to obtain the maximum value in the above systems?

Our experiments were not sufficiently long to capture the maximum SOA particle mass in the single VOC *o*-cresol and binary isoprene / *o*-cresol systems because of logistical constraints.

5) Figure1b&c: Only 6 lines were observed for the 7 experiments.

We thank the reviewer for pointing out our mistake and we have replaced figure 1 with the new one, below.

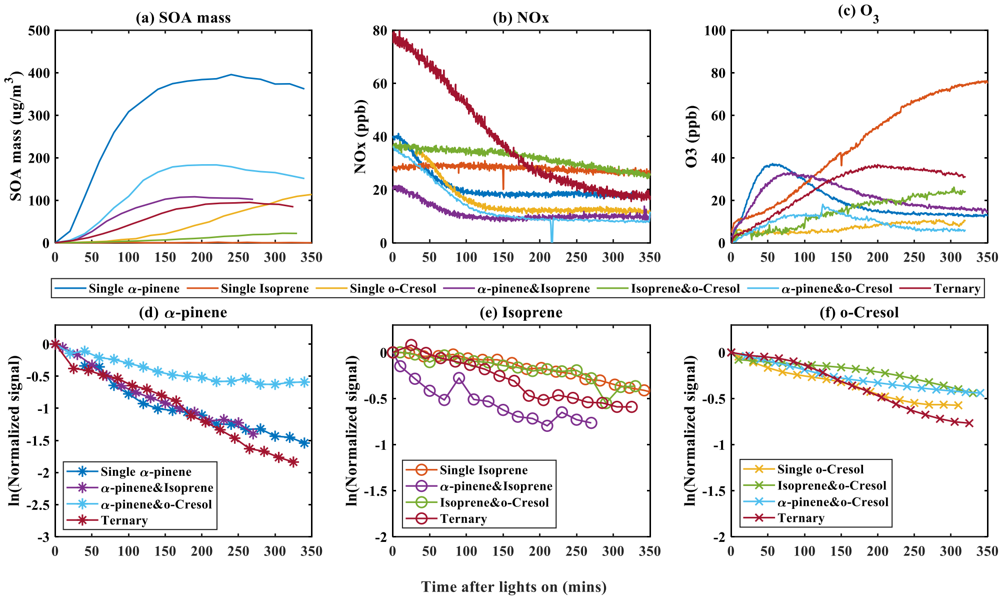

Figure 1：Evolution of gas and total SOA particle mass measurements during the photo-oxidation of VOCs after chamber illumination. (a) The SOA mass was measured using a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) during single, binary and ternary experiment. (b)–(c): Concentration of NO_x and O_3 against time in all of single, binary and ternary experiments. (d)-(f): decay rata of VOC across all systems in. α-pinene (b), isoprene(c) and o-cresol(d) in single, binary and ternary experiments respectively

6) Line 665-668: There is a generally a greater fraction of the positive ionisation mode signal that is inconclusive than in negative ionisation mode. But the explanations are not provided in details.

"Inconclusive" compounds refer to compounds that were detected in only one of the replicate experiments performed for each precursor system in this study. There are several reasons why a compound may not be detected in both replicate experiments. For example, any compounds with a measured peak area close to the limit of detection (defined as 3 × signal-to-noise ratio), a minimum peak intensity below 3×10^4 and that were not detected in three consecutive scans, were removed from the sample data, and subsequently reported as not-detected. These parameters are used for chromatographic peak detection, minimising the detection/inclusion of erroneous background signal. Second, each molecular formula assignment is based on isotopic pattern and abundance scoring, where the theoretical and measured isotopic pattern and abundance are evaluated. Any compound with an isotopic abundance outside of ±30% with a mass tolerance greater than 3 ppm will be removed from the sample data. Further, any compound detected in the sample and chamber background experiment with the same molecular formula and retention time (±0.1) minutes and a sample/chamber background peak area ratio <3 were removed from the sample data. Thus, detected compounds with a measured peak area close to these cut-off values may only be detected in one replicate experiment due to instrumental/experimental variation.

It is worth noting that positive ionisation mode may also be affected by the molecular adduct detected. The non-targeted method cannot detect a sodiated molecular species, if the protonated adduct is not detected (see Pereira et. al (2022) for further information). The protonated molecular species may only represent a small proportion of the measured compound signal and if close to the cut-off values described above, the protonated adduct may not be detected, resulting in the compound being removed from the sample data. This may explain why a greater number of inconclusive compounds were observed in positive rather than negative ionisation mode.

The detailed explanation will be added in line 698: " *.... or a larger fraction of the signal from compounds also found on chamber background filters. Moreover, the greater fraction of "inconclusive" compounds in positive ionization mode might also attributed to automated non-targeted method programming. For example, the automated non-targeted method programmed that compound will be removed from the final detected molecules peak list when they have a signal-to-noise ratio below 3 and low measured signal abundance close to the signal-to-noise cut-off values in the replicate experiment. The automated non-targeted method also programmed the molecular formula assignment base on the isotopic pattern, where the isotopic intensity tolerance was within ±30% of the theoretical isotopic abundance. Consequently, it becomes a challenge to accurately assign a molecular formula to compounds with "large" molecular weights due to arising the number of possible formulars. The "large" compound could have different molecular formula assignments in "representative" and replicate experiments, respectively, though it has a similar retention time and molecular weight in both experiments.* "

7) Results and Discussion: In this study, the molecular structure of the unique compounds or potential tracers were not determined. We know that are some limitations of using nontargeted LC-Orbitrap MS but there are lots of data from gas chromatography mass spectrometer (GCMS), condensation particles counter, differential mobility particle sizer (DMPS) and aerosol mass spectrometer (AMS) (or further detail chemical analysis) which can help to better interpret the results. Even, there is a clear indication of suppression of the yield of α-pinene in its mixture with isoprene in this study, but the explanation/discussion were not sufficient, e.g. why nitrogen-containing species are highly dominant in single cresol oxidation? why greater fraction of the positive ionisation mode signal that is inconclusive than in negative ionisation mode?

This study is part of a more comprehensive study of SOA formation in mixtures, and the scope of this manuscript is to understand the chemical composition and interactions during SOA formation in mixed VOC systems by using offline LC-Orbitrap-MS. Comprehensive information about the suppression of the yield of α-pinene in its mixture with isoprene is presented in Voliotis et al. (2022b), along with the DMPS, GCMS, AMS and FIGAREO-CIMS data in the mixture presented therein. These data are also presented in several companion papers in order to investigate the volatility distribution of products in the mixed system (Voliotis et al., 2021) and explore the chemical compositions in the mixed experiments by the combination of online FIGAERO-CIMS and offline LC-Orbitrap MS measurements (Du et al., 2022). A further study in preparation probes the average carbon oxidation state of SOA in a mixed precursor system by using three different mass spectrometry techniques (AMS, FIAGREO-CIMS and LC-Orbitrap-MS) in order to provide comprehensive insight into the overall effect about molecular interaction impacts the SOA formation and properties. Further explanations about why greater fraction of the positive ionisation mode signal that is inconclusive than in negative ionisation mode will be added in line 673 as mentioned in comment 6 above.

A new section named "3.2.4 Further insight from companion papers" was added in line 1008.

"*This study probes the chemical composition and interactions during SOA formation in mixed VOC systems using the offline LC-Orbitrap-MS technique. The complete instrument description and experimental design is given in Voliotis et al. (2022b), along with the data from online techniques (e.g. SMPS, Semi-continuous GCMS, HR-ToF-AMS and FIGAREO-CIMS). Comprehensive analysis of FIGAERO-CIMS and HR-ToF-AMS data is provided in (Voliotis et al., 2022a; Voliotis et al., 2021; Du et al., 2022). Voliotis et al. (2022a) and Voliotis et al. (2021) investigated the volatility distribution of products in mixed systems using the FIGAERO-CIMS and a thermal denuder coupled with an SMPS and HR-ToF-AMS. Voliotis et al. (2021) reported FIGAERO-CIMS measurements showing an abundance of products uniquely found in the α-pinene / o-cresol mixture, with the majority in the nC=5-10 and nC>10 classes. This result is consistent with the finding in this study that unique compounds were found in α-pinene / o-cresol mixture obtained from LC-Orbitrap-MS measurement , likely the cross-products from α-pinene and o-cresol oxidation in the particle-phase. Voliotis et al. (2021) observed a dominant contribution of nitrogen-containing compounds to the total signal in all o-cresol containing systems, similar to the results obtained from negative ionization mode in LC-Orbitrap-MS in this study. This is unsurprising owing to the high sensitivity of the iodide CIMS towards o-cresol photo-oxidation produced nitro-aromatic compounds with hydroxyl* *groups, such as methyl-nitrocatechol and methyl-nitrophenol (Lee et al., 2014; Iyer et al., 2016).”*

Reference:

Atkinson, R. B., D. L. Cox, R. A.Crowley, J. N.Hampson, R. F.Hynes, R. G.Jenkin, M. E.Rossi, M. J.Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I - gas phase reactions of Ox, HOx, NOxand SOxspecies, Atmos. Chem. Phys., 4, 1738, 10.5194/acp-4-1461-2004, 2004.

Calvert, J. G.: The mechanisms of atmospheric oxidation of aromatic hydrocarbons, Oxford: Oxford University Press, 2002.

Cheng, Y., He, K. B., Duan, F. K., Zheng, M., Ma, Y. L., and Tan, J. H.: Measurement of semivolatile carbonaceous aerosols and its implications: A review, Environment International, 35, 674-681, https://doi.org/10.1016/j.envint.2008.11.007, 2009.

Deng, W., Liu, T., Zhang, Y., Situ, S., Hu, Q., He, Q., Zhang, Z., Lü, S., Bi, X., Wang, X., Boreave, A., George, C., Ding, X., and Wang, X.: Secondary organic aerosol formation from photo-oxidation of toluene with NOx and SO2: Chamber simulation with purified air versus urban ambient air as matrix, Atmospheric Environment, 150, 67-76, https://doi.org/10.1016/j.atmosenv.2016.11.047, 2017.

Du, M., Voliotis, A., Shao, Y., Wang, Y., Bannan, T. J., Pereira, K. L., Hamilton, J. F., Percival, C. J., Alfarra, M. R., and McFiggans, G.: Combined application of Online FIGAERO-CIMS and Offline LC-Orbitrap MS to Characterize the Chemical Composition of SOA in Smog Chamber Studies, Atmos. Meas. Tech. Discuss., 2021, 1-42, 10.5194/amt-2021-420, 2021.

Iyer, S., Lopez-Hilfiker, F., Lee, B. H., Thornton, J. A., and Kurtén, T.: Modeling the Detection of Organic and Inorganic Compounds Using Iodide-Based Chemical Ionization, The Journal of Physical Chemistry A, 120, 576-587, 10.1021/acs.jpca.5b09837, 2016.

Lee, B. H., Lopez-Hilfiker, F. D., Mohr, C., Kurtén, T., Worsnop, D. R., and Thornton, J. A.: An Iodide-Adduct High-Resolution Time-of-Flight Chemical-Ionization Mass Spectrometer: Application to Atmospheric Inorganic and Organic Compounds, Environmental Science & Technology, 48, 6309-6317, 10.1021/es500362a, 2014.

Priego-Capote, F. and Luque de Castro, M. D.: Analytical uses of ultrasound I. Sample preparation, TrAC Trends in Analytical Chemistry, 23, 644-653, https://doi.org/10.1016/j.trac.2004.06.006, 2004.

Subramanian, R., Khlystov, A. Y., Cabada, J. C., and Robinson, A. L.: Positive and Negative Artifacts in Particulate Organic Carbon Measurements with Denuded and Undenuded Sampler Configurations Special Issue of Aerosol Science and Technology on Findings from the Fine Particulate Matter Supersites Program, Aerosol Science and Technology, 38, 27-48, 10.1080/02786820390229354, 2004.

Voliotis, A., Wang, Y., Shao, Y., Du, M., Bannan, T. J., Percival, C. J., Pandis, S. N., Alfarra, M. R., and McFiggans, G.: Exploring the composition and volatility of secondary organic aerosols in mixed anthropogenic and biogenic precursor systems, Atmos. Chem. Phys. Discuss., 2021, 1-39, 10.5194/acp-2021-215, 2021.

Voliotis, A., Du, M., Wang, Y., Shao, Y., Bannan, T. J., Flynn, M., Pandis, S. N., Percival, C. J., Alfarra, M. R., and McFiggans, G.: The influence of the addition of a reactive low SOA yield

VOC on the volatility of particles formed from photo-oxidation of anthropogenic – biogenic mixtures, Atmos. Chem. Phys. Discuss., 2022, 1-30, 10.5194/acp-2022-312, 2022a.

Voliotis, A., Du, M., Wang, Y., Shao, Y., Alfarra, M. R., Bannan, T. J., Hu, D., Pereira, K. L., Hamilton, J. F., Hallquist, M., Mentel, T. F., and McFiggans, G.: Chamber investigation of the formation and transformation of secondary organic aerosol in mixtures of biogenic and anthropogenic volatile organic compounds, Atmos. Chem. Phys. Discuss., 2022, 1-49, 10.5194/acp-2021-1080, 2022b.

Zhao, L., Wang, X., He, Q., Wang, H., Sheng, G., Chan, L. Y., Fu, J., and Blake, D. R.: Exposure to hazardous volatile organic compounds, PM10 and CO while walking along streets in urban Guangzhou, China, Atmospheric Environment, 38, 6177-6184, https://doi.org/10.1016/j.atmosenv.2004.07.025, 2004.