Comment on acp-2021-215
Anonymous Referee #2

Referee comment on "Exploring the composition and volatility of secondary organic aerosols in mixed anthropogenic and biogenic precursor systems" by Aristeidis Voliotis et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-215-RC2, 2021

Review: Exploring the composition and volatility of secondary organic aerosols in mixed anthropogenic and biogenic precursor systems

This manuscript presents chemical and volatility information of SOA formed in a batch reactor from a-pinene, o-cresol and an OH iso-reactive mixture of the two. The chemical composition of individual compounds and bulk chemical properties formed in these systems is contrasted and described using FIGAERO-ToF-CIMS and volatilities are qualitatively described using the FIGAERO-ToF-CIMS and quantified using TD-AMS. This work builds on recent studies highlighting mixed VOC systems cannot be treated as the sum of their single component systems. Mixed SOA products are observed that have an intermediate volatility between the two values of the single component mixtures. This study provides valuable discussion on the differences between SOA produced in single component and mixed systems and expands upon the unknown outcomes of mixed precursor systems. As such, this manuscript should be considered for publication in ACP after addressing the following comments.

The authors would like to thank the reviewer for his/her time and effort to provide constructive comments/suggestions to our work. Your contribution is much appreciated.

Please find below itemised replies to each one of the comments/suggestions.

General Comments

The intent of the manuscript is clear and well contextualised and the descriptions of the experimental conditions are comprehensive. The complexity of the system and the information made available by these measurements means many descriptive details are included, which at times is not presented in the most understandable way. Regarding presentation there are three major points to address:
Sections describing key characteristics of SOA from the different systems in terms of product signal, Mw, C number, O:C and C* (and surrogate temperature ranges) are difficult to follow and should be simplified (e.g. sections 3.2.1 and 4.1). One suggestion might be a graphical summary or table of key findings to use as a reference for the reader to follow. Additionally smaller sections in the larger blocks of text (e.g. 4.1) might also help the reader follow the discussion better.

We thank the reviewer for this suggestion. In the revised manuscript have expressed the results from the FIGAERO-CIMS in the VBS framework using a set of Tmax->Psat calibrations as well as using partitioning calculations. We have further separated the large blocks of text in the discussion Section to smaller parts so it is easier for the readers to follow.

The larger the discussion on sensitivity effects of the FIGAERO-ToF-CIMS on data interpretation (Section 4.2) the more the focus of the manuscript shifts from its original aims. While the discussion is useful and in part necessary, it might be best placed, at least partially, in the supplementary material.

We agree with the reviewer that this part may have been unnecessarily extensive, shifting the main focus of the paper. In the revised manuscript we have shorten the Section 4.2 (Section 4.3 in the revised manuscript).

Despite the detail of the results and discussion, the conclusion is very general and overly simplified. For example, there is no summary of any of the major chemical composition findings or mention of the VOCs used in the experiments. This section would be improved by summarising more of the key findings.

We agree with the reviewer that many of our major findings were lost in the conclusions. In the revised manuscript we have revised the whole conclusions section that now reads as:

“Many climate/air quality prediction models express SOA volatility based on single-precursor experiments and neglecting the potential interactions of the molecules deriving from various precursors that are emitted in the atmosphere and lead to the SOA formation (Yahya et al., 2017; Tsimpidi et al., 2018). However, more and more studies are showing that the results obtained under using single VOC precursor systems, might not represent accurately the ambient atmosphere in which hundreds of VOC are oxidised simultaneously (McFiggans et al., 2019; Shilling et al., 2019). Here, we comprehensively investigate the SOA composition and volatility upon mixing of α-pinene and o-cresol under photo-oxidation conditions, using two independent techniques. Our experimental setup might not fully represent the real atmosphere owing the lack of smaller organic molecules (such as CO or CH4) that may influence the radical termination pathways (Schervish and Donahue, 2020), however provides the grounds to investigate the potential of the molecular interactions to alter the SOA composition and properties in mixtures.

The volatility estimation techniques showed substantial discrepancies in the obtained log10C* values, highlighting the complexity in deriving the volatility distribution and the need for further studies to investigate the thermal evaporation of the organics. However they all showed similar trends; the SOA particle volatility from the photo-oxidation of α-pinene had stronger contributions of higher volatility material compared to that from the o-cresol, while SOA particle volatility of their mixture appeared to be in-between. This was further supported by the qualitative data that are used for the estimation of the
volatility that is the MFR in the TD and the sum thermograms and the partitioning coefficient distribution in the FIGAERO-CIMS. The chemical information obtained enabled us to provide links between the chemical composition and volatility and showed that the extensive fragmentation occurred in the α-pinene system probably resulted in the observed higher volatility SOA. On the other hand, the majority of the particle phase products from the o-cresol were having 6-7 carbon atoms, higher O:C and OSc, potentially explaining their lower volatility. Importantly, our results first show that upon mixing α-pinene and o-cresol there were two opposite effects: first the suppression in the formation of higher MW and lower volatility compounds derived from each individual precursor, that increase the volatility of the mixture and second, the formation of unique products in the mixture that were having lower volatility, higher OSc, O:C and MW that decreased the volatility of the mixture. The trade-off between these two effects could be determining the overall SOA particle volatility in conditions where multiple VOC precursors are reacting simultaneously, where in this case, was found to be in-between those measured in the single precursor experiments.

There is some ambiguity in interpreting the FIGAERO-CIMS data owing to the potential shift of the thermograms due to the different filter loadings and likely, the evaporation behaviour of the compounds in the FIGAERO, as well as the a priori selectivity of the instrument towards certain products, defined by the instrument setup (Lee et al., 2014; Riva et al., 2019). The relative agreement however in the obtained volatility trends between our independent techniques might indicate that the FIGAERO-CIMS, at least qualitatively, could capture the SOA volatility changes in mixed precursor systems and identify corresponding changes in the SOA chemical composition.

The results presented here call for further studies to explore the mechanisms that are driving these observations. Furthermore, studies conducted on various chemical regimes and using various oxidants might improve our understanding about the importance of molecular interactions in mixtures. The formation of new products in mixtures as well as the differential contribution of each precursor’s product to the particle phase implies a range of potential changes on the SOA properties and thereby their subsequent interactions of the SOA with water vapour and other particles and gases (Champion et al., 2019; Riipinen et al., 2015; Pankow et al., 2015). Further, the potential effect of mixing anthropogenic and biogenic products might significantly affect the predicted SOA radiative forcing (Gordon et al., 2016; Kelly et al., 2018)."

Additionally some sentences are missing words or are badly formulated which should be corrected with a read through.

We thank the reviewer for pointing this out. A thorough English language check was performed in the whole manuscript.

Specific Comments

1) Line 26: 37% and 39% are very close, is there an error estimate to say how different these figures really are?

Indeed, these figures were quite similar. The errorbars shown on Fig. 5 of the original manuscript (Fig. 4 in the revised manuscript) were representing the model uncertainty. This has been clarified in the revised manuscript. The whole results and discussion Sections have been adjusted based our new approach to show the volatility distributions from the FIGAERO-CIMS to the VBS framework and the abstract has been changed accordingly.
2) Like 70: “ultra-low volatility” vs extremely low volatility

The correction has been made in the revised manuscript.

3) Line 90 (and 141): For context, put numbers on the SOA yields in main text (not just low, moderate, high).

Indicative yields have been added in both sentences in the revised manuscript (L93-96 and L146-147) as:

“This choice of precursors and contributory reactivities enabled investigation of SOA formation with mixed systems containing a low, a moderate and a high yield precursor (i.e., isoprene; 0-4%; Carlton et al. (2009), o-cresol; 7-12%; Smith et al. (1998) and α-pinene; 20-30%; Eddingsaas et al. (2012a), respectively) with equal initial chances of reacting with the dominant oxidant and equal contributions of first-generation oxidation products.”

And

“Here, we focus on the α-pinene and o-cresol system, as representative biogenic and anthropogenic VOC precursor sources (Hallquist et al., 2009; Schwantes et al., 2017), both with appreciable SOA yields (7-30%; e.g., Henry et al., 2008; Eddingsaas et al., 2012a).”

4) Line 128: What is electronic capture device grade? Is there a purity associated with that?

We use N4.8 ECD grade nitrogen with purity 99.998%. This has been included in the revised manuscript (L134).

5) Line 147 – 152: It would be helpful to include an equation to demonstrate the iso-reactive conditions in the chamber (i.e. concentrations and reaction rates).

Indeed, an equation might be beneficial to the readers (eq. 1). This has been included in the revised manuscript (L166).

6) Line 175: Is there a difference between e.g. experiments 1-4 or are these repeats? Should reacted VOC be included as well (for those interested in yields)?

The experiments conducted under the same conditions are indeed repeats. This has been clarified in the revised manuscript as:

“As shown in Table 1, a number of repeat experiments were conducted for each system in order to increase our confidence in the validity of our results as well as to overcome technical difficulties due to instrument failures over certain experiments (see Table S1).”

Further, the VOC consumptions are given in the Fig. S10 in the revised SI.

7) Line 214: How were line losses minimised by using 2m long PTF tubing and a 2 sL min⁻¹ flow?
PTFE tubing is considered more appropriate for sampling gases compared to stainless steel tubing, while our sample flow rate results in a residence time of the sample of ~<2 s, which is lower than the recommended times by the US EPA (20 s; USEPA, 2011). Nonetheless, it is true that in our case, it is unknown whether the line losses were minimised. In the revised manuscript, we omitted this statement and the sentence is now reads as:

“The gas phase was sampled through a separate line, using a 2 m long, ¼-inch PTFE tubing (Sulyok et al., 2002; Mittal et al., 2013) at 2 sL min⁻¹ that results in a sample residence time of <~2s”

8) Line 217: What is the significant of the “known concentration mix”?

Indeed, the known concentration mix is insignificant here. The sentence has been changed in the revised manuscript (L253-255) as:

“The reagent ions were produced by passing a mix of CH₃I and UHP N₂ over a ²¹⁰Po radioactive source and passed directly into the IMR.”

9) Line 217: Formatting ²¹⁰Po

We thank the reviewer for pointing out this typo. The correction has been made in the revised manuscript.

10) Line 244: You only mass calibrate to 381 m/z but peak fit up to 550 m/z, how confident are you of the peak fitting accuracy beyond 381 if you have no higher mass calibrant?

We agree with the reviewer that any peak assignment above 381 m/z can be erroneous. Nonetheless, in all the experiments conducted the fraction of the signal in the >381 m/z region was <2% of the total particle phase signal and <1% of the total gas phase signal indicating that any assignment in that region would have negligible effect in the reported results expressed as signal fraction.

11) Line 246: Why Kendrick mass defect and not just mass defect?

We agree with the reviewer that it is no longer necessary to state “Kendrick’s” mass defect, so in the revised manuscript the word “Kendrick’s” was omitted from the sentence.

12) Line 248: What interferences occur during the soak period? Does this affect your integrations?

We agree that the word “interferences” might not be appropriate in this context. The soak period is designed to ensure that any remaining organic compounds would have been desorbed from the filter and that the filter is “clean” for the next cycle. In order to integrate the signals during the desorption cycle a linear increase in the desorption temperature is required (e.g., Buchholz et al., 2020), therefore the measurements conducted during the soak period were not included here. We have altered the wording of the original sentence to read as:
Further, note that only the particle phase data collected during the temperature ramp were considered here as the integration of the data requires a linear increase in the desorption temperature (e.g., Buchholz et al., 2020).

13) Line 265: Typically particle phase backgrounds have been reported using a preconditioned filter (e.g. Bannan et al., 2019) or passing the sample through a filter to remove aerosol (e.g. Lutz et al., 2019). The method described here is unusual and I am uncertain it would capture correctly the instrument response. A background desorption cycle is needed.

We appreciate that our initial description might not been adequate in this section. Similarly to Bannan et al., 2019 and to Lutz et al., 2019, a background desorption cycle was performed in each experiment and subtracted from the measurements. Particularly, the desorption cycle obtained during the “dark unreactive” phase, where only VOC, NOx and seed in the absence of light was used a background correction cycle. We have clarified this in the revised manuscript (L303-305) as

“Subsequently, the integrated area of each peak measured during the FIGAERO-CIMS desorption cycle during “dark unreactive” phase (see Section 2.2; Fig. S5a) was subtracted from the data to remove any seed and/or filter effect.”

14) Line 305: Is the word total correct? Sum of gas and particle?

We see the confusion that these statements might have caused. We have altered all of our statements in the revised manuscript to explicitly state whether the total signal corresponds to the gas or particle phases.

15) Line 328: Does the O:C calculated for figure 2 only account for CHO compounds? Are you more confident that the sensitivity of the CHO is not as variable as CHON?

The O:C in this figure was calculated for all the products identified (ie both the CHO and CHON) and was weighted to the signal of each compound to the particle phase. This has been clarified in the revised manuscript as:

“Figure 2 shows the average (± 1σ) O:C ratio of all the products identified in each system from the FIGAERO-CIMS in the particle phase, weighted to the contribution of each product to the total particle phase signal, along with O:C ratio derived from the HR-AMS.”

16) Line 342: Did you try applying gas/particle partitioning to derive C* from the FIGAEROToF-CIMS? This section I find difficult to follow because there is so much information, particularly the description of figure 4. I find the inserted bar chart contains more interesting information than the three main pie charts. Would you better express your point if you had a relative signal fraction as well as the absolute signal fraction in the bar chart? Also the temperature ranges and their corresponding descriptions are mixed, and confused with general descriptions of volatility e.g. 90°C = “less volatile” but later within this section terms like ‘low volatility’ are used which I don’t think are meant to refer to these ranges. Perhaps using the temperature ranges or acronyms might better separate these categories from general descriptions as well as the rationale for their use.
We agree with the reviewer that the selected presentation of the results in the original manuscript might have been difficult to follow and the limits that were chosen to represent the more or less volatile fraction were, more or less, arbitrary. There are multiple ways to derive the C* from the FIGAERO-CIMS, such as the gas/particle partitioning, using explicit Tmax->Psat calibrations with compounds with known vapour pressures (e.g. Bannan et al., 2019) or by using empirical formulations (e.g. Mohr et al., 2019). In the revised manuscript we have expressed the volatility distributions derived from the FIGAERO-CIMS in the VBS framework using Psat-Tmax calibrations as well as from partitioning calculations and we discuss the implications of the selected method to the results in the Section 4.1. In this way, we avoid the general descriptions of volatility and we use the well-established VBS framework to discuss our results. Particularly, the volatility distributions derived from the FIGAERO-CIMS in the mixed VOC system are separated to show the contributions from the products of either precursor, the common, as well as those that were unique to the mix (see Fig. 3 in the revised manuscript). Furthermore, additional figures (see Fig. 6 and 7 in the revised manuscript) were made and to illustrate the effect of each category of compounds to the volatility of the mixture.

17) Line 380: The unidentified fraction grows for the >90°C mixed system. Do you state what these might be e.g. inorganics, sampling artefacts, deprotonated organics? You should be more explicit in how you define the signals you have investigated i.e. I- adducts and/or deprotonated and what atoms you consider (CHON etc.). It might be that the unknown signal is an unimportant grouping and better removed as you are only interested in the identifiable CHO and CHON I- adducts.

We agree with the reviewer that the unidentified fraction could induce further complications to our analysis and deviate the manuscript of its main goals i.e., to link the SOA composition and volatility.

After interrogating our unidentified fraction, it appears that a considerable fraction of it (~up to 50%) is composed by ions barely above or below our detection ability (i.e., signal to noise ratio ≤2) Consequently, also in line with your suggestion, we have decided to exclude the unidentified fraction from our analysis and focus the revised paper on the identified fraction.

18) Line 426: “…volatile SOA particles from the o-cresol system are considerably more oxygenated compared to the average than those of the a-pinene system”. This statement is a good example of an interesting finding being lost in the discussion and conclusion.

We agree with the reviewer that in the original manuscript some of the interesting results were lost in the discussion and conclusion. These sections have been revised to emphasise the main results.

19) Line 426: Figure 6. Why are the gradient terms of the lines of best fit negative?

The gradients of these lines on figure 6 of the original manuscript (Fig. 5 of the revised manuscript) are negative as the x-axis is plotted in reverse order (MFR=1->0).
20) Line 432: As no volatilities are derived from the FIGAERO-ToF-CIMS, this might be a good section to explain why you are comparing C* derived from the TD with qualitative descriptions of volatility from FIGAERO-ToF-CIMS. Can you comment on any discrepancies between TD measurements up to 90°C vs FIGAERO-ToF-CIMS up to 200°C? Some qualification on their comparison would be useful for the reader to assess the differences in information these similar techniques provide.

We agree that this approach was not adequate and these temperature limits were more or less arbitrary. It is very difficult to relate the desorption of the compounds in the FIGAERO-CIMS with the evaporation of the SOA in ~30s in the TD. In the revised manuscript we have expressed the FIGAERO-CIMS results to the VBS framework so a related comparison can be achieved in an established classification system.

21) Line 474: "Their relatively low contribution to the total FIGAERO-CIMS signal might indicate that they will make little contribution to the mass of the C*≤1 µg m⁻³...". Generally I would be careful equating uncalibrated CIMS signal directly to mass and focus more on the relative differences between the cases.

We agree that this comparison might sound misleading, given that our CIMS was uncalibrated. Due to the change of the results and discussion, this sentence no longer exists in the revised manuscript. Nonetheless, we have soften such arguments throughout the revised manuscript.

22) Line 478: OH addition or abstraction?

As has been observed previously (Schwantes et al., 2017; Olariu et al., 2002), the main oxidation pathway of o-cresol leading to ring-retaining products proceeds through the OH addition and H abstraction to form a dihydroxy toluene (C7H8O2).

23) Line 489: What is the “formula separation technique” here referring to?

Our formula separation technique refers to our method to identify the compounds that are deriving of each precursor, are common or unique in the mixture (as stated in the Methods section). This has been clarified in the revised manuscript (L307-320) and a supporting flow chart has been added (Fig. S7 in the revised SI).

24) Line 499, 510: What is meant by the word “bulk” in these contexts?

In the sentence in the L499 of the original manuscript the bulk was defined as the sum of the “individual precursor’s plus common products in the mixture” (shown in brackets).

25) Line 506: These descriptions of high O:C, high desorption temperatures and lower volatility are too vague.

The discussion has been changed in this section owning to the different analysis conducted expressing the FIGAERO-CIMS results in the VBS framework.
26) Line 519: This appears to be a key finding missed from the conclusion.

We agree with the reviewer that this might have been lost in the conclusions. The conclusions section has been revised to include this information.

27) Line 526: Discussion of signal contributions throughout this section is confusing e.g. it does not feature in figure 7; is it that important to mention here? If it is, can it be discussed separately or reformulated?

According to the reviewer’s major comments, this section has been split into subsections (now Section 4.2.1 and 4.2.2), while additional figure have been created so it easier to follow.

28) Line 585: This section focuses on I- CIMS sensitivity differences to the presence of nitrate functional groups (as this has been shown to impact sensitivity by up to two orders of magnitude). The variation in sensitivity between CHO compounds can also be 2-3 orders of magnitude (Aljawahry et al., 2013), which could also affect the thermogram shapes in a similar way. Should CHO compounds be considered similarly to CHON in this calibration sensitivity test?

We agree that with the reviewer that the sensitivity of the CHO is equally important to the CHON. Given the overwhelmingly higher amount of particle phase signal observed from the C7H7NO4 in the o-cresol system defining the shape of the volatility distribution, along with the very high contribution of CHON, our intention with this exercise was to assess the potential role of the sensitivity towards the CHON group.

According to the reviewer’s major comments, this section has been shorten and this exercise has been omitted from the revised manuscript as it was deviating the manuscript from its original scope that is to provide links between the chemical composition and volatility in mixed precursor systems.

39) Line 630: These points are difficult to follow. What does “average” refer to?

Owing to the different representation of the results and discussion these statements have been altered in the revised manuscript (L808-814) as:

"The SOA particle yield from the o-cresol experiments was found to be modest (14±3%), while that from the α-pinene considerably higher (27±4%; Fig. S18), suggesting that the observed domination of the o-cresol products in the mixed systems is unlikely. Considering further the relative agreement between the FIGAERO-CIMS and the TD and the analysis presented above (Sections 4.1-4.2), we can argue that the SOA particles in the mixture, are composed by the products of the higher yield precursor (i.e., α-pinene) with considerable contributions of the o-cresol derived products, as well as those deriving from the mixing of the two precursors.”
References

Aljawhary, D., Lee, A. K. Y. and Abbatt, J. P. D.: High-resolution chemical ionization mass spectrometry (ToF-CIMS): application to study SOA composition and processing, Atmos. Meas. Tech., 6(11), 3211–3224, doi:10.5194/amt-6-3211-2013, 2013.

Bannan, T. J., Le Breton, M., Priestley, M., Worrall, S. D., Bacak, A., Marsden, N. A., Mehr, A., Hammes, J., Hallquist, M., Alfarra, M. R., Krieger, U. K., Reid, J. P., Jayne, J., Robinson, W., McFiggans, G., Coe, H., Percival, C. J. and Topping, D.: A method for extracting calibrated volatility information from the FIGAERO-HR-ToF-CIMS and its experimental application, Atmos. Meas. Tech., 12(3), 1429–1439, doi:10.5194/amt-12-1429-2019, 2019.

Lutz, A., Mohr, C., Le Breton, M., Lopez-Hilfiker, F. D., Priestley, M., Thornton, J. A. and Hallquist, M.: Gas to particle partitioning of organic acids in the boreal atmosphere, ACS Earth Sp. Chem., 3(7), 1279–1287, doi:10.1021/acsearthspacechem.9b00041, 2019.

References

Buchholz, A., Ylisirniö, A., Huang, W., Mohr, C., Canagaratna, M., Worsnop, D. R., Schobesberger, S., and Virtanen, A.: Deconvolution of FIGAERO–CIMS thermal desorption profiles using positive matrix factorisation to identify chemical and physical processes during particle evaporation, Atmos. Chem. Phys., 20, 7693-7716, 10.5194/acp-20-7693-2020, 2020.

Kendrick, E.: A Mass Scale Based on CH2 = 14.0000 for High Resolution Mass Spectrometry of Organic Compounds, Anal Chem, 35, 2146-2154, 10.1021/ac60206a048, 1963.

Mittal, L. A., Green, D. C., Sweeney, B. P., Quincey, P. G., and Fuller, G. W.: Sampling system influence on gaseous air pollution measurements, Atmos Environ, 79, 406-410, 10.1016/j.atmosenv.2013.06.051, 2013.

Mohr, C., Thornton, J.A., Heitto, A. et al. Molecular identification of organic vapors driving atmospheric nanoparticle growth. Nat Commun 10, 4442 (2019). https://doi.org/10.1038/s41467-019-12473-2

Olariu, R. I., Klotz, B., Barnes, I., Becker, K. H., and Mocanu, R.: FT-IR study of the ring-retaining products from the reaction of OH radicals with phenol, o-, m-, and p-cresol, Atmos Environ, 36, 3685-3697, Pii S1352-2310(02)00202-9. Doi 10.1016/S1352-2310(02)00202-9, 2002.

Schwantes, R. H., Schilling, K. A., McVay, R. C., Lignell, H., Coggon, M. M., Zhang, X., Wennberg, P. O., and Seinfeld, J. H.: Formation of highly oxygenated low-volatility products from cresol oxidation, Atmospheric Chemistry and Physics, 17, 3453-3474, 10.5194/acp-17-3453-2017, 2017.

Sulyok, M., Haberhauer-Troyer, C., and Rosenberg, E.: Observation of sorptive losses of volatile sulfur compounds during natural gas sampling, J Chromatogr A, 946, 301-305, Doi 10.1016/S0021-9673(01)01541-2, 2002.

US EPA, 2011. Code of Federal Regulations. Title 40, Part 58, Appendix E.9.