

Atmos. Chem. Phys. Discuss., referee comment RC2  
<https://doi.org/10.5194/acp-2021-215-RC2>, 2021  
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## Comment on acp-2021-215

Anonymous Referee #2

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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

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### **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  $\alpha$ -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.

#### **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,  $M_w$ , 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.
- 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.

- 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.

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

### **Specific Comments**

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

Line 70: "ultra-low volatility" vs extremely low volatility

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

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

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).

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)?

Line 214: How were line losses minimised by using 2m long PTF tubing and a 2 sL min<sup>-1</sup> flow?

Line 217: What is the significant of the "known concentration mix"?

Line 217: Formatting <sup>210</sup>Po

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?

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

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

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.

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

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?

Line 342: Did you try applying gas/particle partitioning to derive C\* from the FIGAERO-ToF-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.

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<sup>-</sup> 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<sup>-</sup> adducts.

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.

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

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.

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<sup>-3</sup>...". Generally I would be careful equating uncalibrated CIMS signal directly to mass and focus more on the relative differences between the cases.

Line 478: OH addition or abstraction?

Line 489: What is the "formula separation technique" here referring to?

Line 499, 510: What is meant by the word "bulk" in these contexts?

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

Line 519: This appears to be a key finding missed from the conclusion.

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?

Line 585: This section focuses on I<sup>-</sup> CIMS sensitivity differences to the presence of nitrated 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 (Aljawhary 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?

Line 630: These points are difficult to follow. What does "average" refer to?

## 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., Mehra, 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.