

## Response to comments of anonymous referees # 1

The paper summarizes average carbon oxidation states of SOA formed from photooxidation of single and mixture VOCs (o-cresol,  $\alpha$ -pinene, and isoprene) in the presence of NO<sub>x</sub>. SOA were sampled online by HR-ToF-AMS and FiGAERO-I-CIMS and offline by HPLC-MS to determine the average oxidation state of carbon. Results from different experiments and instruments were then compared to investigate how the chemistry of SOA formation is influenced by the presence of another precursor.

We kindly thank the reviewer for their time and effort in providing comments for our manuscript. Please see our responses below (shown in blue).

There are two other papers from the group which apparently have highlighted already what the common and unique SOA products are in these systems. I therefore don't know what the value of this paper is in addition to the more robust identified products in their previous work.

As the authors highlight, HR-ToF-AMS cannot provide an accurate estimate of the average OSc since it cannot determine the N-content of aerosols well. FIGAERO and HPLC-MS are each sensitive to certain classes of compounds and so don't provide a complete picture of the oxidation products either. That said, I think there is value in comparing results from one instrument across the single/mixture systems to say something about the differences in chemistry. I therefore believe the manuscript can eventually be published, but it needs major revisions in my opinion. As is, there are simple conclusions that are hidden in the paper and lost in the mere numeric comparisons presented in Sections 3 and 4. Please see below my comments:

We thank the reviewer for this insightful comment and for recognizing the relevance of our study to the group's earlier work. We fully agree that previous publications from our group have focused on compound level identification of SOA products formed from single and mixed precursor systems. However, the present manuscript provides distinct and complementary findings, in quantitatively comparing the average carbon oxidation state (OSc) and chemical evolution patterns of SOA across different precursor systems and analytical techniques (HR-ToF-AMS, FIGAERO-CIMS, and UHPLC-HRMS), providing insight into bulk oxidation trends linked to underlying chemical mechanisms.

To clarify this novelty of this work, we have substantially rewritten the Results, Discussion, and Conclusion sections to explicitly frame the study around five guiding research questions:

- i. *“How does  $\overline{\text{OSc}}$  vary with SOA mass loading to provide insights into volatility and aging process?”*
- ii. *How do different initial precursor reactivities influence  $\overline{\text{OSc}}$  evolution in single precursor experiments?*

- iii. *How consistent are  $\overline{\text{OSc}}$  estimates across different analytical techniques, and what does the respective bias imply.*
- iv. *How do the nitrogen-containing compounds affect the  $\overline{\text{OSc}}$  estimation, particularly in systems that contain abundant CHON products?*
- v. *How does the mixing of precursors impact on the oxidation trajectories compared to the single precursor system, using  $\overline{\text{OSc}}$  as a diagnostic metric?*

General comments:

Experimental section: The experimental section early on should mention that NO<sub>x</sub> was adjusted to keep the VOC/NO<sub>x</sub> ratio the same. What's the predicted average OH in the expts?

We appreciate the reviewer for pointing out that the predicted average OH concentration in the experiments should be mentioned.

We included this in section 2.1:

*From line 192-196: "The average OH concentration during illumination was estimated from the decay rates of solely OH-reactive VOCs (e.g., o-Cresol), yielding a concentration of approximately  $1 \times 10^6$  molecules  $\text{cm}^{-3}$ . This OH source arose from O<sub>3</sub> generated via NO<sub>2</sub> photolysis, which was further photolysed in the moist chamber atmosphere."*

Sections 3.1-3.3 read as sentences comparing average OSc estimates from one condition/instrument to the next and is not that valuable as written. For example, I didn't get a sense of what to think about the different estimates or sometimes opposing trends in the estimates from the positive vs. negative ion modes of HPLC-MS. I think for this section to be useful, the data need to be better synthesized and a summary presented in a way different than just comparing pairs of average OSc values.

We appreciate the reviewer for this constructive comment. We agree that the original Results section (Sections 3.1–3.3) was overly descriptive and focused mainly on numerical comparisons between experiments and instruments, which limited its interpretative value. In the revised manuscript, these sections have been condensed and reorganised to improve readability and flow.

Specifically, the text has been shortened to highlight the main trends in the evolution of OSc across precursor systems, rather than listing numerical comparisons between instruments. To reduce redundancy, the HR-ToF-AMS data for the multi-VOC systems were removed, while the AMS results for the single  $\alpha$ -pinene and o-Cresol experiments were retained to demonstrate the comparison among the three mass spectrometric techniques (HR-ToF-AMS, FIGAERO-CIMS, and UHPLC-HRMS) in estimating OSc which directly addresses Question 3 of the study aims.

In the previous version, each system included four panels showing OSc, O:C, H:C, and N:C as a function of SOA mass. In the revised version, only the OSc versus SOA mass plots are retained in the main text to emphasise the core result, while the atomic ratio plots (O:C, H:C, N:C) have been moved to the Supplementary Information. This restructuring reduces repetition and focuses the Results on the most relevant trends, while still providing the complete dataset in the SI for reference.

Section 4: I was hoping this section contains a more synthesized look at the data, but it's a summarized set of comparisons again (without actually mentioning all the OSc values) and the discussion is more on limitations of the instruments (or preferential detection of certain compounds) rather than actual chemistry

Since there is evidence for nitrogen-containing ions to be formed in these systems and OS of nitrogen has a significant impact on the estimated average OSc, I don't see the value in comparing OSc when OS of nitrogen is ignored, so in my mind, the data from HR-ToF-AMS should not be included in the paper and any other reference to average OSc disregarding OS of nitrogen should be removed.

We appreciate the reviewer's valuable comment. We agree that the earlier version of the *Discussion* section was primarily descriptive and focused on instrument-specific limitations. In the revised manuscript, this section has been rewritten to provide a more integrated interpretation of the results and to explicitly summarise key findings. The discussion now links OSc evolution across single and mixed precursor systems to underlying chemical mechanisms, focusing on how precursor reactivity, mixture interactions, and nitrogen-containing compounds influence the oxidation trajectories of SOA formation.

In response to the reviewer's suggestion, we have introduced a new summary table (Table 2) in section 4.4 that synthesises the average OSc estimated both *accounting for* and *not accounting for* the oxidation state of nitrogen ( $OS_n$ ). This table highlights how including  $OS_n$  consistently lowers the calculated OSc, particularly in the o-Cresol system where CHON products dominate, while the effect is smaller in  $\alpha$ -pinene experiments. These comparisons quantify the systematic bias introduced when  $OS_n$  is neglected and provide a concise overview of inter-instrument consistency, directly addressing the reviewer's request for a more synthesised presentation of results.

Regarding the inclusion of HR-ToF-AMS data, we appreciate the reviewer's concern about its inability to account for the  $OS_n$ . In the revised manuscript, AMS results are only retained for the single  $\alpha$ -pinene and o-Cresol systems and are used solely for methodological comparison with FIGAERO-CIMS and UHPLC-HRMS. Including the AMS data is essential for demonstrating how different analytical techniques, each with distinct detection sensitivities, influence the estimated average OSc when analysing the bulk SOA products from the same

experiment. The AMS results are therefore presented not as core chemical findings, but as a diagnostic benchmark for evaluating inter-instrument consistency, directly addressing one of the study aims (Question 3). In particular, it will provide valuable insight into the limitations of the use of the AMS for deducing oxidation state when it may be the sole mass spectrometric instrument used in a study.

Specific comments:

P3, L63: add some reference for recent research on multi-VOC systems

Additional references on recent research involving multiple VOC systems have been added in Introduction 1 line 46 “(Han et al., 2025; Chen et al., 2025; Cui et al., 2024)”

P3, L29-71: consider breaking this sentence to multiple or rephrase it for ease of readability

The sentence has been rephrased for improved readability and now appears in lines 51–54 of the revised manuscript:

*“Mcfiggans et al. (2019) demonstrated that isoprene reduced SOA mass and yield by scavenging OH radicals and their derived products, thereby suppressing the formation of highly oxygenated molecules (HOMs) from  $\alpha$ -pinene oxidation and increasing the overall volatility of the mixture.”*

L 264: C in DeCarlo should be capitalized

The reference has been corrected accordingly.

L 265 Reference to Sueper doesn't need the first name initial

The reference has been corrected accordingly.

L294: how long was sonication done?

The text has been revised accordingly. The sentence in lines 283–285 now reads:

*“1) Filter samples were dissolved in 4 mL of LCMS-grade methanol, left to stand for 2 hours at ambient temperature, and then extracted using sonication for 30 minutes (Fisher Scientific FB15051).”*

L299: evaporation to dryness was carried out at a much warmer temperature than room. What's the potential impact in driving off some of the more volatile SOA components?

We have now addressed this in the Methods section by acknowledging the potential loss of volatile components during the evaporation step. The revised text (lines 289–292) reads:

*“The evaporation step may result in the partial loss of the most volatile SOA components; however, most LCMS detectable species are low-volatility and thus retained under these conditions.”*

L499: change significantly to significant

L639: remove either “in” or “for”

L770: delete “which”

L833: what do you mean by “at a higher magnitude”?

L928: delete “be”

We thank the reviewer for these detailed editorial suggestions. These five line-specific comments have been addressed, as the corresponding sections (*Results*, *Discussion*, and *Conclusion*) were substantially rewritten and reorganised in the revised manuscript. The sentences referenced by these line numbers no longer appear in their original form.

L962 and 949: there are two contradictory statements on the average OSc of the mixture in these two statements

The section containing these contradictory statements has been removed in the revised manuscript. The discussion of the ternary  $\alpha$ -pinene/o-Cresol/isoprene system has been fully rewritten under the new section “4.2 Influence of precursor mixture on average OSc during SOA formation.” The revised text (lines 660–684) now provides a consistent and mechanistically grounded interpretation, explaining that the ternary system exhibits intermediate OSc values resulting from competing chemical processes, including OH scavenging by isoprene, enhanced  $\text{RO}_2 + \text{NO}$  reactions, and cross-interactions among precursor-derived radicals.

Reference:

Chen, X., Li, K., Li, R., Fang, L., Bian, H., Jiang, W., Yan, C., and Du, L.: NO<sub>x</sub>-driven chemical transformation of terpene mixtures: Linking highly oxygenated organic molecules to health effects in secondary organic aerosol, *Journal of Environmental Sciences*, <https://doi.org/10.1016/j.jes.2025.09.004>, 2025.

Cui, Y., Chen, K., Zhang, H., Lin, Y.-H., and Bahreini, R.: Chemical Composition and Optical Properties of Secondary Organic Aerosol from Photooxidation of Volatile Organic Compound Mixtures, *ACS ES&T Air*, 1, 247-258, 10.1021/acsestair.3c00041, 2024.

Han, S., Li, Z., Lau, Y. S., Xiao, Y., Miljevic, B., Horchler, J., Li, J., Hu, W.-P., Wang, H., Wang, B., and Ristovski, Z.: Unraveling secondary organic aerosol formation from isoprene and toluene mixture, *npj Climate and Atmospheric Science*, 8, 311, 10.1038/s41612-025-01189-4, 2025.

McFiggans, G., Mentel, T. F., Wildt, J., Pullinen, I., Kang, S., Kleist, E., Schmitt, S., Springer, M., Tillmann, R., and Wu, C.: Secondary organic aerosol reduced by mixture of atmospheric vapours, *Nature*, 565, 587, 2019.

## Response to comments of anonymous referees # 2

This manuscript describes results from environmental chamber experiments in which VOCs (single VOCs, and binary and ternary mixtures) were reacted with OH to form secondary organic aerosol (SOA). In particular, this paper focuses on the oxidation state of carbon (OSc) of the SOA formed, measured with three different instruments: a HR-ToF-AMS, FIGAERO-CIMS (both online methods) and UHPLC-HRMS (an offline method). A chief complication in comparing OSc from these three instruments is that they all measure it imperfectly – the HR-AMS cannot quantify nitrogen (N) accurately, and the other two methods are selective, i.e. do not detect all organic compounds. This paper presents a thorough discussion of oxidation state measured by the different instruments during the different experiments, but for me as a reader I had difficulty following the main scientific takeaways from these measurements, especially considering the caveats of the oxidation state measurements. A thus suggest major revisions of this manuscript.

We kindly thank the reviewer proving the throughout feedback for our manuscript. We agree that, in the original version, the main scientific takeaways were not presented clearly enough, and the discussion of OSc across the three instruments could be difficult to follow given their differing sensitivities and measurement limitations. In response, the manuscript has been extensively revised and restructured to clarify its scientific objectives and highlight the core conclusions. The revised Introduction section now explicitly outlines the five guiding research questions that frame the analysis, providing a clearer flow for the reader. The Results and Discussion sections have been reorganised/re-written to follow this structure, with simplified descriptions, and clearer transitions between instruments (Further details on the revisions to the Results and Discussion sections are provided below).

### General comments:

I find this paper difficult to follow in part due to the amount of quantitative information described in the results section. Perhaps some of these results could be presented in tabular format so that the text can focus more on trends and discussion (rather than numbers). I also suggest that the authors highlight the main results / scientific insights from the study in the revised version of the manuscript.

We thank the reviewer's helpful suggestions. We agree that the original Results section contained excessive quantitative detail, which may have made it difficult for readers to identify the main scientific insights. The revised result sections now removed the HR-ToF-AMS data of the mixed precursor systems, as these were largely redundant and did not provide additional insights relevant to the study objectives. The atomic ratio (O:C, H:C, N:C) plots versus SOA mass for individual mixed precursor systems have also been moved to the *Supporting Information*, while only the OSc evolution of each precursor system is retained in the main text, since these represent the core results addressing the guiding research questions.

Furthermore, the revised Discussion now synthesises how differences in instrument selectivity, precursor initial reactivity, and nitrogen content influence the estimated OSc values. A new summary table (Table 2) has been added to quantify the effect of including or excluding the OSn, directly illustrating how such methodological differences contribute to systematic offsets

between instruments. The key takeaways are now clearly stated in the Conclusions section, emphasising (i) how OSc evolution offers insight into the underlying chemical processes governing SOA formation and aging (ii) the consistency of OSc trends across single and mixed precursor systems, (iii) the impact of accounting for nitrogen-containing compounds, and (iv) the complementary nature of online and offline mass spectrometric techniques in constraining SOA oxidation chemistry.

We believe these revisions improve the clarity, focus, and interpretative strength of the manuscript, addressing the reviewer's concern and making the main scientific insights more accessible.

Lines 195-203: It is unclear to me how the chamber background and experimental background were subtracted from the data, and how this may impact reported measurements of oxidation state from the three different instruments. Perhaps a more detailed explanation in the SI would help, with graphs showing background, experimental data, and corrected data.

We appreciate the reviewer pointing out that the procedure of chamber and experimental background subtraction is not clear. A detailed description of the background subtraction procedures for each instrument has been added to the Supplementary Information (Section S1). This section now explains how both the chamber and experimental backgrounds were treated for the FIGAERO-CIMS, UHPLC-HRMS, and HR-ToF-AMS datasets. For FIGAERO-CIMS and UHPLC-HRMS, the procedures are described in detail following established methods from Voliotis et al. (2021) and Pereira et al. (2021). For HR-ToF-AMS, we have also included an example time series (Fig. S1) illustrating the chamber background period and confirming that organic mass and elemental ratios remained stable before SOA formation. These additions clarify the background correction process and ensure transparency in how the OSc values were derived for each instrument.

#### Specific comments

Line 52-53: The last sentence of the abstract is unclear, especially the phrase "to enable... atmosphere". Please revise.

We appreciate the reviewer's helpful comment. The abstract has been fully revised, and the final sentence has been removed in the revised version.

Line 316-317: "Thus, produced product ion spectrum, to inform the compound's structural characterisation and isomer identification" Please revise the sentence – unclear.

The sentence had been revised to "*The resulting product ion spectra were then used to support structural characterisation and isomer identification of the compounds*" in line 309 to 310.

Line 792-793: "experiments, suggesting that the dominant control by  $\alpha$ -pinene oxidation products (Fig.2a)." Revise this sentence (remove "that"?)

Line 795-797: "However, the magnitude of average OSc in mixture system is slightly lower than in the single  $\alpha$ -pinene experiment, the influence of isoprene oxidation products on the

average carbon oxidation state of total SOA.” Please revise this sentence (especially the second phrase) – unclear.

Line 797-799: “Isoprene is known to form C4 and C5 compounds with high volatility (e.g. methacrolein (C4) and C5-hydroxycarbonyls) on OH oxidation, with potential to suppress the particulate mass form from  $\alpha$ -pinene oxidation in the mixed system.” Please revise, unclear.

We appreciate the reviewer’s detailed feedback on the clarity of this subsection. The portion of the Discussion referring to the  $\alpha$ -pinene/isoprene binary system has been fully rewritten in the revised manuscript to improve readability and scientific precision. The new text (lines 565-588) now provides a clearer description of the observed OSc trends and the underlying chemistry interpretation, replacing the previously ambiguous sentences. The revised paragraph distinguishes more explicitly between the roles of  $\alpha$ -pinene and isoprene-derived products and explains how their interaction affects SOA oxidation state and composition.

There are other grammar issues throughout the manuscript, e.g. missing periods.

The entire manuscript has been carefully proofread, and all grammatical errors, including missing periods and typographical issues, have been corrected in the revised version.

Reference:

Pereira, K., Ward, M., Wilkinson, J., Sallach, J., Bryant, D., Dixon, W., Hamilton, J., and Lewis, A.: An Automated Methodology for Non-targeted Compositional Analysis of Small Molecules in High Complexity Environmental Matrices Using Coupled Ultra Performance Liquid Chromatography Orbitrap Mass Spectrometry, Environmental Science & Technology, 10.1021/acs.est.0c08208, 2021.

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.