Supplement of Aerosol Research, 3, 619–636, 2025
https://doi.org/10.5194/ar-3-619-2025-supplement

*Supplement of*

# The evolution of carbon oxidation state during secondary organic aerosol formation from individual and mixed organic precursors

**Yunqi Shao et al.**

*Correspondence to:* Gordon McFiggans (g.mcfiggans@manchester.ac.uk)

## 1. Background Subtraction Procedures for LC–HRMS, FIGAERO–CIMS, and HR-ToF-AMS

### (A) FIAGERO-CIMS

The FIGAERO-CIMS particle-phase data used in this study were pre-processed as part of the companion analysis of the same mixture VOC system experiments. Only the particle-phase products were used here. Background subtraction was applied in two steps following the procedure described in Voliotis et al. (2021) :

1. **Instrument background correction**

For each desorption cycle, the 60–90 s interval after switching to particle mode (with desorption temperature < 22 °C, and avoided the “noisy” signal produced by the ion molecule reaction (IMR) chamber pressure change) was used as an “instrument background.” The average signal from this period was subtracted from the raw particle-phase desorption data.

2. **Chamber background correction.**

Integrated particle-phase peaks were further corrected by subtracting signals measured during the dark unreactive phase (i.e., before lights on), to account for seed and filter contributions and any background compounds not attributable to photochemistry.

The resulting background-corrected peak lists (molecular formulas and integrated signal intensities) were provided to us and used directly for calculation of H:C, O:C, and $\overline{OSc}$. Full details of the background subtraction method are available in Voliotis et al. (2021).

### (B) UHPLC-HRMS

To account for potential artefacts introduced by the chamber environment, we analyzed Teflon filters collected during dedicated chamber background experiments ($O_3$ photolysis with lights on for 6 h, or off-gassing without $O_3$). In both cases, particle mass remained ≈0 μg $m^{-3}$, but filters were collected and analyzed identically to SOA samples to provide a chamber background reference.

Automated non-targeted data analysis was performed using Compound Discoverer 2.1 (Thermo Fisher Scientific), following the approach validated in Pereira et al. (2021). This method extracts chemical features from each UHPLC–HRMS data file, assigns molecular formulae based on accurate mass and isotopic patterns, and removes compounds present in procedural blanks. The output is a list of detected compounds with molecular formulae, retention times, and signal intensities for each sample (see Pereira et al., 2021 for full details and validation).

Data treatment first established a set of "common products" by requiring compounds to be detected in at least two replicate SOA experiments with consistent molecular formula and retention time within ±0.1 min. The resulting compound lists were then compared against the temporally nearest chamber background experiment. Features with matching molecular formula and retention time ($\Delta RT \leq 0.1$ min) were evaluated based on their relative intensities: compounds with a sample-to-background peak area ratio $\geq 3$ were retained as genuine SOA products, with intensities corrected by subtraction of the background signal ($I_{corr}=I_{SOA}-I_{BG}$) whereas compounds with ratios $<3$ were excluded. This combined reproducibility and background correction procedure ensured that only robust, reproducible products significantly above the chamber background were included in the final dataset, thereby minimizing artefacts and cross contamination.

## (C) HR-ToF-AMS

For HR-ToF-AMS, we did **not** subtract a separate chamber background from the elemental ratios. Instead, we verified that during the 1 hour “chamber background period (All reactants present in the chamber bag including the seed particles under dark condition) period”, the organic mass concentration was at or near the detection limit (~0 µg $m^{-3}$) and both H/C and O/C remained stable. Because subtracting a mean from ratios in a regime where Org ≈ 0 would amplify noise without changing subsequent values once SOA mass developed, we retained the Igor-processed data directly (m/z calibration, baseline fit, HR fragment analysis) for calculating H/C, O/C, and OSc=2(O/C)−H/C. An example time series is shown in Fig. S1, confirming negligible particulate background prior to illumination.

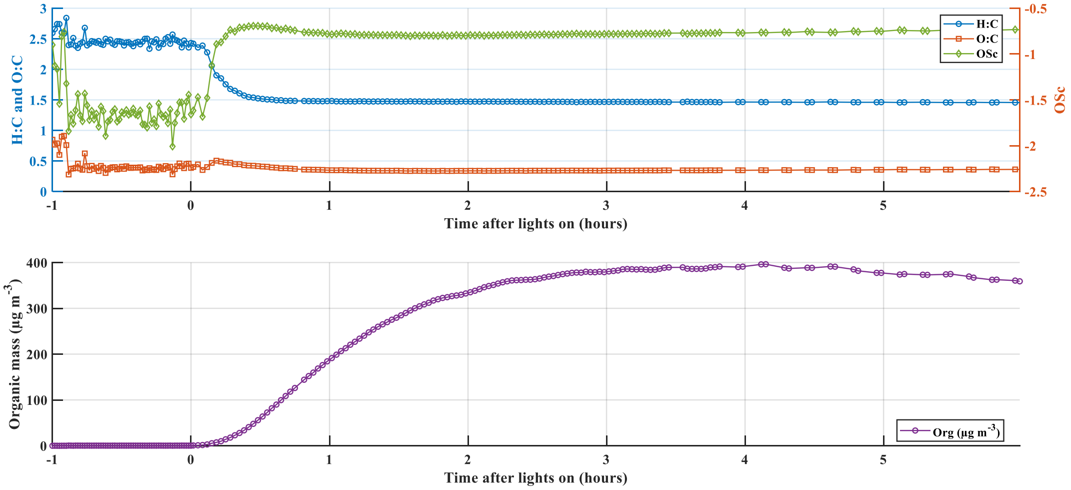

**Figure S1.** Time series of H:C, O:C, and $\overline{OSc}$ from HR-ToF-AMS for single full reactivity α-pinene experiment. Data gaps later in the experiment correspond to periods when the AMS was bypassed to sample through a thermal denuder for a parallel measurement; these points were removed from the analysis.

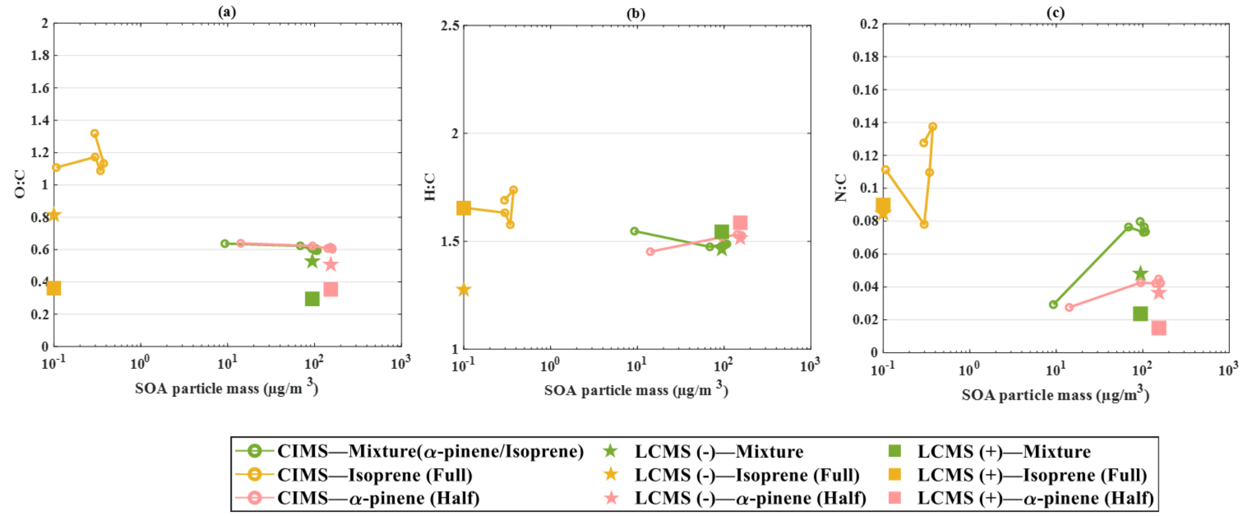

Figure S2: Evolution of atomic ratios with SOA mass in the α-pinene/isoprene system: (a) O:C, (b) H:C, and (c) N:C. Results from FIGAERO-CIMS (lines) and UHPLC-HRMS (symbols; negative ion mode = stars, positive ion mode = squares)

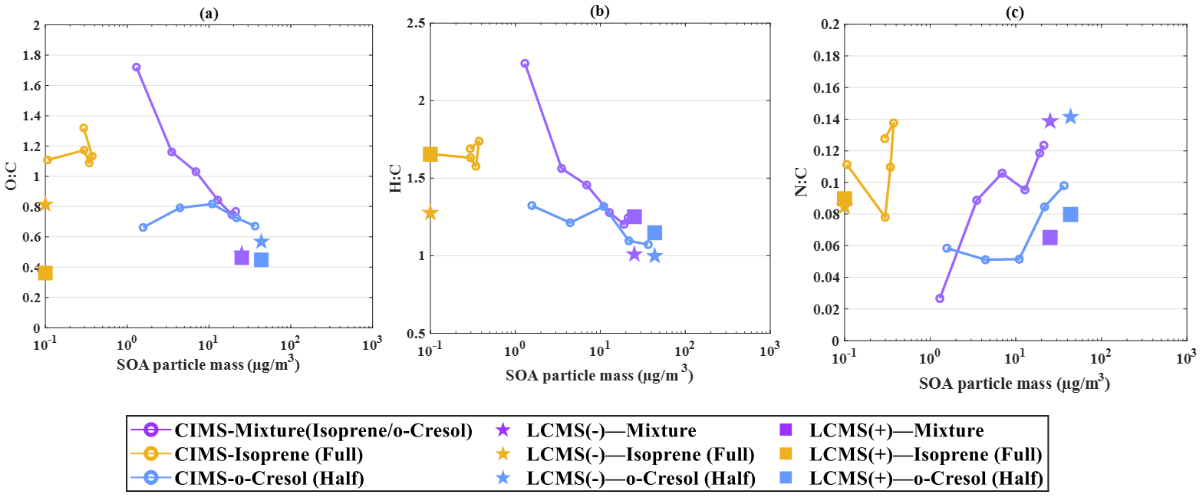

Figure S3: Evolution of atomic ratios with SOA mass in the o-Cresol/Isoprene system: (a) O:C, (b) H:C, and (c) N:C. Results from FIGAERO-CIMS (lines) and UHPLC-HRMS (symbols; negative ion mode = stars, positive ion mode = squares)

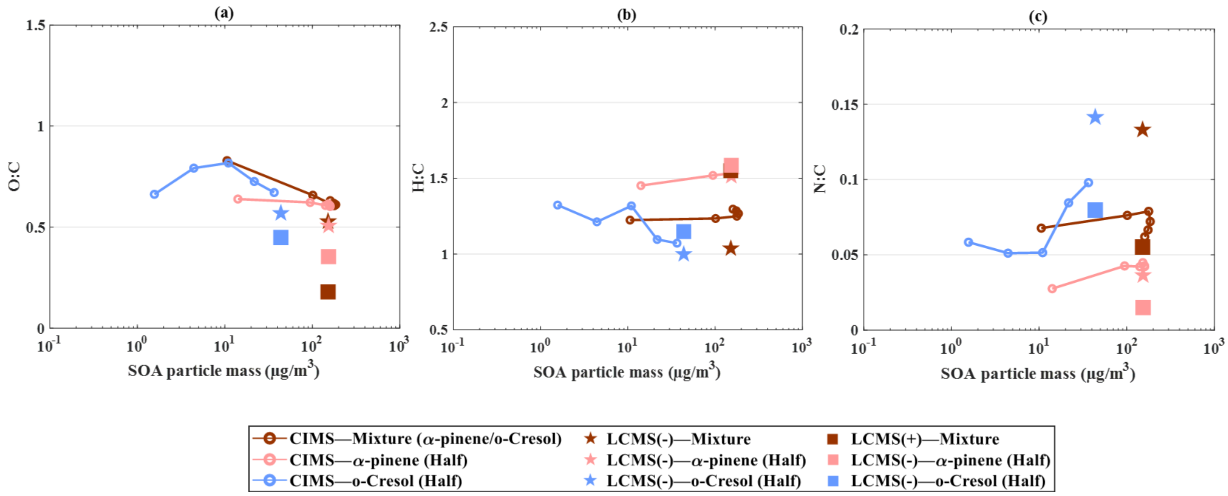

Figure S4: Evolution of atomic ratios with SOA mass in the α-pinene/o-Cresol system: (a) O:C, (b) H:C, and (c) N:C. Results from FIGAERO-CIMS (lines) and UHPLC-HRMS (symbols; negative ion mode = stars, positive ion mode = squares)

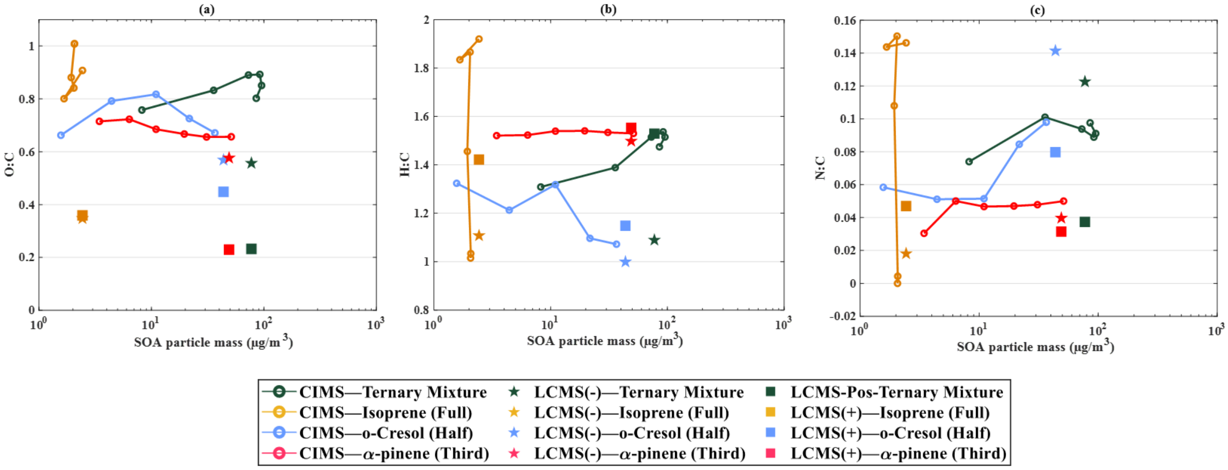

Figure S5: Evolution of atomic ratios with SOA mass in the α-pinene/isoprene/o-Cresol ternary system: (a) O:C, (b) H:C, and (c) N:C. Results from FIGAERO-CIMS (lines) and UHPLC-HRMS (symbols; negative ion mode = stars, positive ion mode = squares)

## 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.