

This manuscript presents a field application of VIA-NO₃-CIMS at SORPES to characterize particle-phase OOMs and explore their potential source/process contributions. The dataset is interesting, and the combination with AMS measurements could provide useful molecular-level insight into SOA composition. However, several central interpretations are currently not sufficiently supported. In particular, the source-oriented PMF factor names, the non-concurrent gas-particle comparison, and the quantitative interpretation of VIA-NO₃-CIMS signals require substantial clarification. I recommend major revision before the conclusions on particle-phase OOM sources and gas-particle differences can be accepted.

Response: We sincerely thank the reviewer for the careful evaluation and constructive comments. We agree that several interpretations in the original manuscript, particularly the source-oriented PMF factor names, the comparison of non-concurrent gas- and particle-phase measurements, and the quantitative interpretation of VIA-NO₃-CIMS signals, required further clarification and more cautious wording. In response, we have substantially reorganized the PMF interpretation, added analyses to evaluate the representativeness of the gas-phase reference dataset, expanded the characterization of temperature-dependent molecular composition, and clarified the semi-quantitative nature and methodological limitations of the concentration estimates. Our point-by-point responses are provided below, and corresponding changes made in the manuscript and Supplementary Information are marked in yellow.

Major comments

Reviewer: The PMF factor names “biogenic-dominated” and “anthropogenic-dominated” are too strong. The authors acknowledge that PMF factors are mixed and not pure source categories. After applying the DBE-Oeff screening, the contribution of the biogenic-related factors is also substantially reduced, from about 51% in the PMF factors to 37%. Have the authors checked whether the biogenic ions enhanced in the PMF factors are consistent with the molecular classification criteria used in Nie et al. 2022? If not, the factors should be renamed more conservatively.

In addition, two factors with pronounced daytime peaks are both classified as biogenic factors. I do not think AVOC oxidation during daytime can be ignored. The authors should justify why these daytime factors are assigned mainly to biogenic sources rather than mixed BVOC/AVOC photochemical SOA.

Response: Thank you for this important and constructive comment. We agree that the original factor names “biogenic-dominated” and “anthropogenic-dominated” were too source-specific for PMF factors containing chemically mixed molecular components.

As you suggestion, the two factors have been renamed Daytime OOM-1 and Daytime OOM-2. The three nighttime factors have likewise been renamed Nighttime OOM-1, Nighttime OOM-2, and Nighttime OOM-3. The remaining factors are termed Regional Background OOM and Pollution-

Episode OOM. These revised names describe the dominant temporal or atmospheric characteristics of the factors without imposing unique precursor-source assignments. The revised factor names and corresponding interpretations are provided in Sect. 3.3.1 (Lines 576-845) of the revised manuscript. The corresponding figure labels, captions, and descriptions in the Supplementary Information have also been updated.

We also agree that AVOC oxidation during daytime cannot be excluded. The pronounced daytime maxima of the two factors indicate their association with daytime photochemical processing but do not uniquely identify their precursor sources. Daytime oxidation at the SORPES site may involve both BVOCs and AVOCs, and the resulting oxidation products may subsequently undergo gas-particle partitioning and multiphase processing. We therefore cannot justify assigning these two factors exclusively or predominantly to biogenic precursors.

In Nie et al., (2022), a practical challenge is to separate Monoterpene-OOMs from aromatic-OOMs, which share $n_{O,eff}$ and DBE with the same range. Nie et al., (2022) assigned monoterpene-OOMs based on their PMF results, and the residual peaks were further classified according to the DBE- O_{eff} screening. This challenge applies also to our study – monoterpene-OOMs and aromatic-OOMs cannot be separated purely by the chemical formula, and this is probably the reason why we have overlooked the AVOC OOM in the daytime.

To further characterize the molecular composition of the seven PMF-resolved factors, we revised the molecular-classification framework used in the manuscript (Fig. S36). First, a literature-based list was compiled from previous laboratory and field studies reporting molecular formulas associated with the oxidation of isoprene, monoterpenes, and sesquiterpenes through OH-, O_3 -, and NO_3 -initiated pathways. Molecular formulas included in this list were classified as literature-supported BVOC-related OOMs, regardless of the PMF factor in which they occurred. The representative formulas, proposed precursors and oxidation pathways, measurement phases, and corresponding references are summarized in Table S2.

Molecular formulas not included in the literature-based list were subsequently classified according to their double-bond equivalents. Compounds with $DBE < 2$ were categorized as aliphatic-like OOMs, those with $2 \leq DBE \leq 4$ as aromatic-like OOMs, and those with $DBE > 4$ as polyaromatic-like OOMs. The same procedure was applied independently to all seven PMF factors, including Regional Background OOM and Pollution-Episode OOM. PMF factor identity, temporal behavior, and correlations with atmospheric proxies were not used as molecular-classification criteria.

After weighting the molecular-class fractions within each factor by the corresponding PMF factor contributions, literature-supported BVOC-related OOMs accounted for 12.1% of the total PMF-resolved particle-phase OOM signal (Fig. 7). The operationally classified AVOC-related OOMs accounted for the remaining 87.9%, including 4.0% aliphatic-like, 41.2% aromatic-like, and 42.7% polyaromatic-like OOMs. Thus, molecular formulas assigned to the aromatic-like and polyaromatic-like classes dominated the PMF-resolved signal under the adopted classification framework. Literature-supported BVOC-related OOMs were distributed across all seven factors rather than being confined to a single PMF component, while every factor contained multiple molecular classes. This distribution further demonstrates that the PMF factors represent mixtures of temporally covarying compounds rather than chemically pure precursor categories.

This classification should be regarded as an operational framework rather than a definitive source-apportionment method. Its interpretation relies largely on the current understanding of gas-phase OOM composition and the relationships between molecular formulas and VOC precursors (Nie et al., 2022). However, the particle-phase OOMs measured in this study may have undergone gas–particle partitioning, accretion or oligomerization, hydrolysis, further oxidation, and other multiphase transformations after their initial formation. These processes can alter their molecular formulas and DBE values, thereby weakening the relationship between the detected particle-phase composition and the original VOC precursors. In addition, the literature-based BVOC list is incomplete and biased toward commonly studied precursors and reaction systems. BVOC oxidation products absent from the list may therefore be classified as AVOC-related, whereas formulas reported in BVOC oxidation systems may also be produced from anthropogenic precursors because the same molecular formula can represent multiple isomers and formation pathways. The BVOC- and AVOC-related fractions should therefore be interpreted as operationally classified molecular-signal fractions rather than definitive source contributions, and the direction and magnitude of the overall classification bias cannot be quantitatively determined. Detailed descriptions of the molecular classification method and results are provided in Sect. 3.3.2 (Lines 914–977) of the revised manuscript and Sect. S10 (Lines 602–636) of the Supplementary Information.

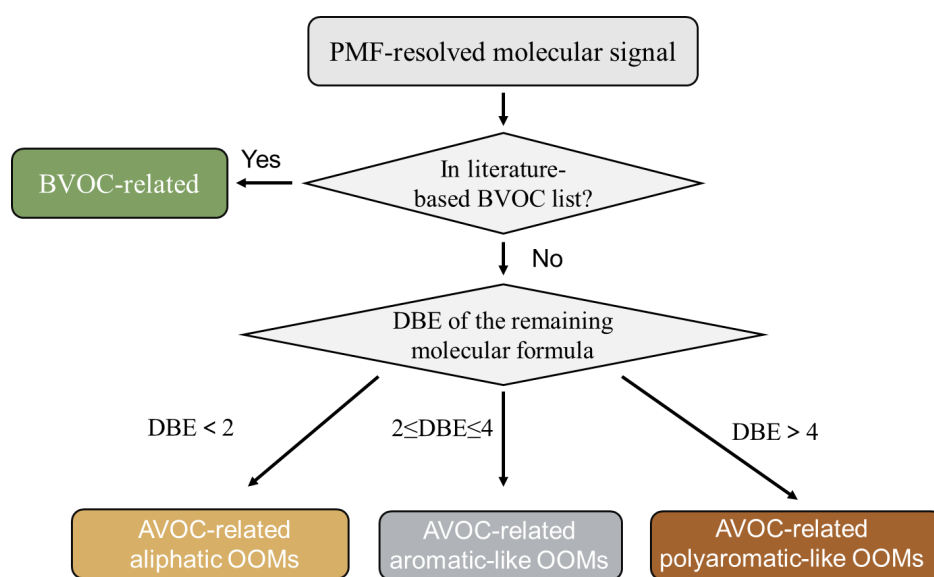


Figure S36. Sequential workflow used to classify molecular formulas within the seven PMF-resolved particle-phase OOM factors. Formulas included in the literature-based BVOC oxidation-product list were classified as literature-supported BVOC-related OOMs. The remaining formulas were grouped according to their double-bond equivalents as aliphatic-like OOMs ($\text{DBE} < 2$), aromatic-like OOMs ($2 \leq \text{DBE} \leq 4$), or polyaromatic-like OOMs ($\text{DBE} > 4$). The same procedure was applied independently to all seven PMF factors.

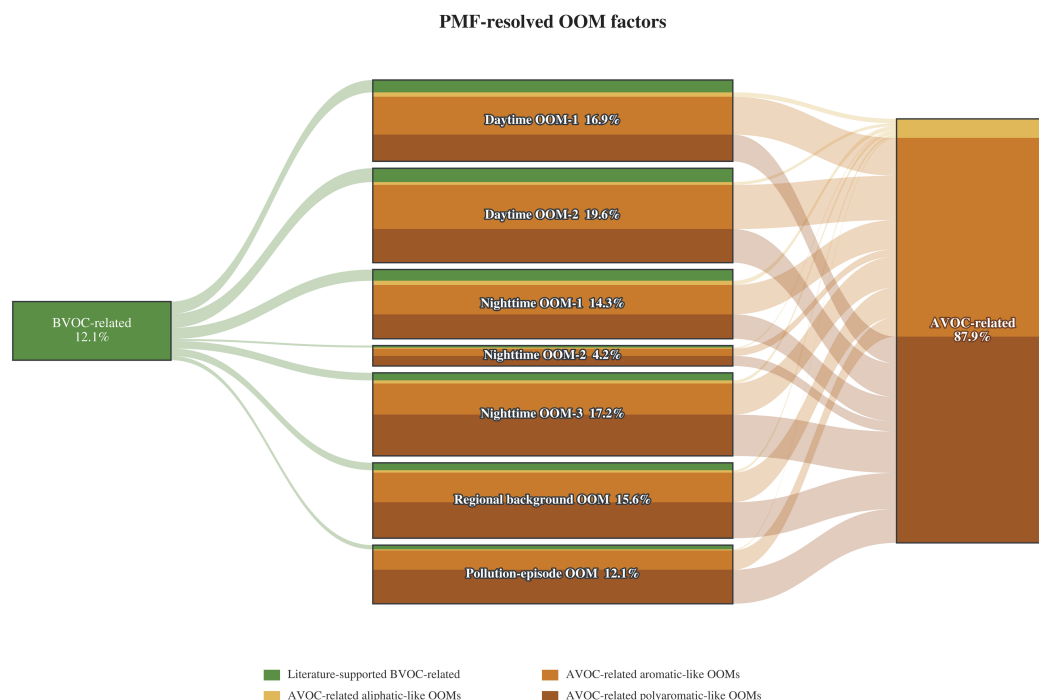


Figure 7. Molecular-level classification of the seven PMF-resolved particle-phase OOM factors. Molecular formulas were classified using a literature-based BVOC list and DBE-based criteria for the remaining AVOC-related OOMs. Ribbon widths represent contributions to the total PMF-resolved OOM signal. Percentages in the central and side nodes indicate the contributions of individual PMF factors and the summed BVOC- and AVOC-related fractions, respectively. Detailed classification criteria are provided in Supplementary Information Sect. S10.

Reviewer: The particle-phase OOMs were measured in 2024, whereas the gas-phase OOM reference dataset appears to be from 2022. This makes several gas-particle comparisons rather weak. Similar meteorology alone is not enough to prove that gas-phase HOM/OOM composition was stable across years. If the authors can show multi-year evidence that gas-phase composition is seasonally reproducible, the comparison would be more convincing. The measurement years should also be clearly marked in Figs. 2 and 3 and in their captions to avoid misunderstanding. The Supplement also contains apparent 2022/2023/2024 inconsistencies that need correction.

Since VIA-NO₃-CIMS uses the same nitrate CIMS principle as gas-phase HOM measurements, the authors should also explain why switching or bypass measurements were not available during the 2024 campaign.

Response: Thank you for raising this important concern. We agree that similarity in meteorological conditions alone is insufficient to demonstrate that the detailed molecular composition of gas-phase OOMs remained unchanged between different measurement years. We have therefore further evaluated the representativeness of the available gas-phase measurements and clarified the purpose

and limitations of the gas–particle comparison.

First, we compared gas-phase OOM datasets obtained during four campaigns conducted at the SORPES station in autumn 2022, summer 2023, and spring and winter 2025. All datasets were processed using consistent molecular-screening and signal-normalization procedures. Their relative-intensity distributions were compared as functions of carbon number, nitrogen number, effective oxygen number, and DBE. As shown in the newly added Sect. S7.1 (Lines367-396) and Fig. S18, the summer 2023 dataset exhibited a distinctly higher contribution from C_5 and isoprene-related OOMs, consistent with enhanced isoprene emissions and oxidation during the warm season. Apart from this expected seasonal feature, the four datasets showed broadly comparable distributions of the other gas-phase OOMs in terms of carbon number, nitrogen number, effective oxygen number, and DBE, although the relative intensities of individual molecular classes varied. These results indicate that the gas-phase OOM composition at the SORPES station retained expected seasonal signatures while exhibiting broadly reproducible molecular characteristics across the investigated campaigns.

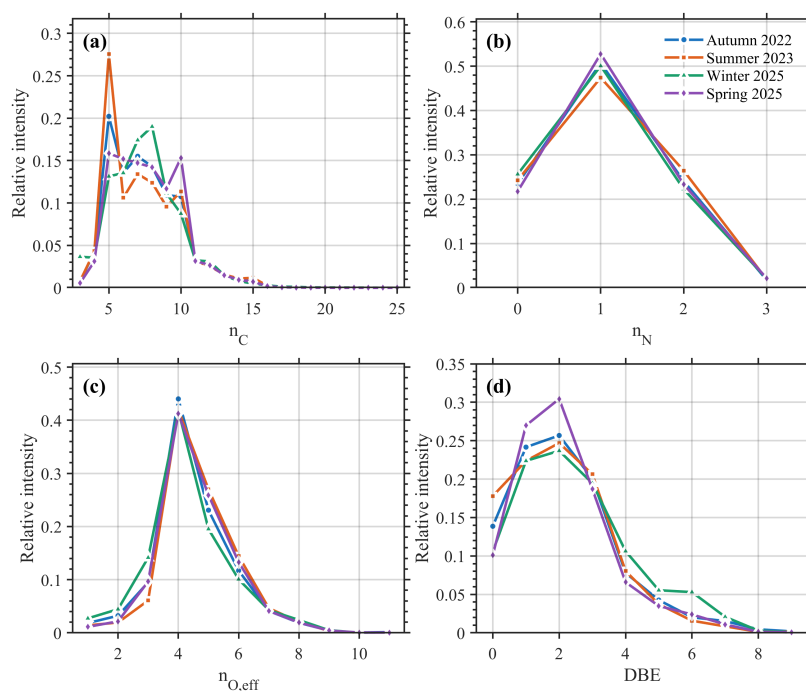


Figure S18. Multi-season and multi-year comparison of the molecular-composition distributions of gas-phase OOMs measured at the SORPES station. Relative-intensity distributions of gas-phase OOMs as a function of (a) carbon number (n_C), (b) nitrogen number (n_N), (c) effective oxygen number ($n_{O,eff} = n_O - 2n_N$), and (d) double-bond equivalents (DBE) during autumn 2022, summer 2023, winter 2025, and spring 2025. Signal intensities were normalized separately for each campaign.

Among the available datasets, the autumn 2022 campaign provided the closest seasonal correspondence with the autumn 2024 particle-phase campaign. To further assess their comparability, we compared the distributions of $PM_{2.5}$, O_3 , and temperature during the two periods. As shown in the newly added Sect. S7.2 (Lines397-420) and Fig. S19, the two campaigns exhibited broadly comparable distributions of these parameters, with substantial overlap in their respective ranges. Together with their seasonal correspondence and the broadly reproducible gas-phase

molecular characteristics observed across the four campaigns, after accounting for expected seasonal features such as the enhanced isoprene-related OOM contribution in summer, these similarities support the selection of the autumn 2022 dataset as the most seasonally relevant gas-phase reference available for the present analysis.

It should be noted that the autumn 2022 dataset is used only to examine broad differences between the campaign-averaged gas- and particle-phase molecular distributions. It is not considered a reconstruction of the exact gas-phase composition present during autumn 2024. Accordingly, this comparison is not used to diagnose instantaneous gas-particle equilibrium, establish direct molecular correspondence between the two phases, or derive compound-specific partitioning coefficients. We have clarified the scope and limitations of this comparison throughout the revised manuscript.

Regarding the absence of switching or bypass measurements, the inlet used during the 2024 campaign was equipped with an activated-carbon denuder upstream of the VIA to remove gas-phase compounds before the particles entered the thermal-desorption unit. Consequently, the measurement configuration used in this study was designed specifically for particle-phase sampling and could not measure ambient gas-phase OOMs directly. Gas-phase measurements would have required a separate inlet or a dedicated bypass upstream of the denuder.

Although VIA-NO₃-CIMS and direct gas-phase NO₃-CIMS use the same ionization chemistry, implementing reliable switching between these two sampling configurations presents substantial physical and instrumental challenges. OOMs are particularly susceptible to inlet and wall losses, while particle-phase VIA sampling and direct gas-phase sampling require different inlet structures, tubing dimensions, flow rates, residence times, and transport conditions. Switching between the two configurations without dedicated optimization and characterization could therefore introduce substantial and compound-dependent transmission artifacts, making direct comparison of the gas- and particle-phase signals difficult.

During the 2024 campaign, such a dual-phase switching or bypass system had not yet been sufficiently developed and characterized. We therefore prioritized stable, continuous particle-phase measurements and did not conduct routine switching between gas- and particle-phase sampling. This limitation is now acknowledged in the revised manuscript, and the development of a carefully characterized system for concurrent gas- and particle-phase measurements is identified as an important direction for future work.

OOMs are particularly susceptible to inlet and wall losses, while particle-phase VIA sampling and direct gas-phase sampling require different inlet configurations, tubing dimensions, flow rates, residence times, and transport conditions. Switching between these configurations without dedicated optimization could therefore introduce substantial and compound-dependent transmission artifacts, making direct comparison of the gas- and particle-phase signals difficult. During the 2024 campaign, a dual-phase switching system had not yet been sufficiently developed and characterized. This limitation is now acknowledged in the revised manuscript, and the development of a carefully characterized system for concurrent gas- and particle-phase measurements is identified as an important direction for future work. These revisions are described in Sect. 3.2.2 (Lines 457-475) of the revised manuscript and Sects. S7 (Lines 367-396) of the Supplementary Information. The

measurement years have also been clarified in Figs. 4 and S19 and their captions, and the inconsistent year labels in the Supplementary Information have been corrected.

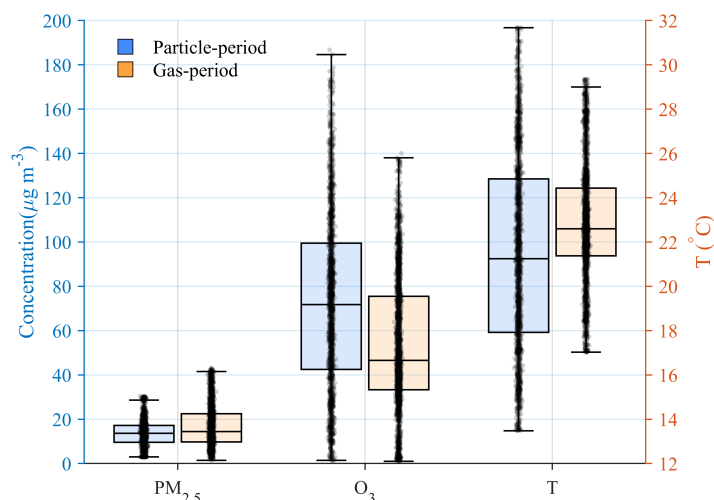


Figure S19. Comparison of atmospheric conditions during the selected gas- and particle-phase measurement periods. Distributions of PM_{2.5}, O₃, and temperature during the gas-phase OOM campaign conducted at the SORPES station from 11 to 25 September 2022 (orange) and the particle-phase OOM campaign from 17 September to 11 October 2024 (blue). PM_{2.5} and O₃ correspond to the left axis, and temperature corresponds to the right axis.

Reviewer: Line 165: The use of SMPS volume loss to infer organic volatilization is not fully convincing, because ambient particles contain both organic and inorganic components. For example, NH₄NO₃ can evaporate readily, whereas sulfate is much less volatile. Since AMS was operated in parallel, why did the authors not use AMS to measure the change in organic mass during VIA heating directly? A component-resolved check would be more appropriate than SMPS volume loss alone.

Response: Thank you for this important suggestion. We agree that measuring the aerosol composition upstream and downstream of the heated VIA using an AMS would provide a more direct and component-resolved assessment than particle-volume measurements alone. Such an experiment would help distinguish the volatilization behavior of organic aerosol from that of inorganic components such as nitrate and sulfate.

Unfortunately, this component-resolved experiment was not included in the instrument-characterization measurements conducted for the present study. Although the AMS was operated concurrently during the field campaign, it sampled ambient aerosol through an independent inlet and was not configured to alternate between the upstream and downstream flows of the VIA. Consequently, the available AMS data cannot be used retrospectively to determine the component-specific changes induced by VIA heating.

We have therefore revised the interpretation of the SMPS experiment rather than treating it as a direct measurement of organic volatilization efficiency. The corresponding text in the revised

manuscript has been revised in Sect. 2.2.1 (Lines 201–211), as follows:

The apparent particle-volume loss at 300 °C was additionally evaluated using size-selected ambient aerosol particles. Particles with diameters between 50 and 470 nm were selected using an aerodynamic aerosol classifier (AAC), and their volume distributions with and without heating were measured using a scanning mobility particle sizer (SMPS). The apparent particle-volume-loss fractions ranged from approximately 70% to 92%, depending on particle size (Fig. S3). Because the ambient particles contained both organic and inorganic components and because physical transmission losses cannot be completely separated from volatilization, these measurements were used only to characterize the overall system response. They were not treated as compound-specific organic volatilization efficiencies and were not used to correct the VIA-NO₃-CIMS concentrations.

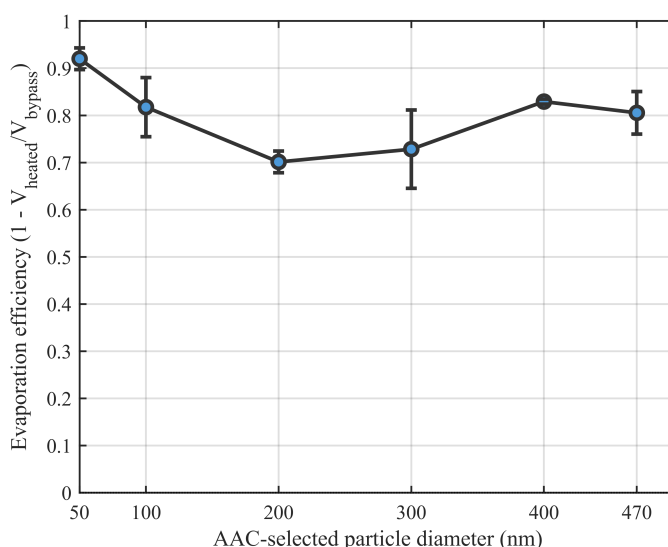


Figure S3. Size-dependent apparent particle-volume-loss fraction at 300 °C. Ambient aerosol particles were size-selected using an aerodynamic aerosol classifier, and their downstream particle-volume distributions under heated and unheated conditions were measured using an SMPS. The apparent particle-volume-loss fraction was calculated as $1 - V_{heated}/V_{reference}$. Error bars represent the variability among repeated measurements. Because ambient aerosol contains both organic and inorganic components and is subject to physical transmission losses, the measured fraction should not be interpreted as the compound-specific volatilization efficiency of particle-phase OOMs.

Reviewer: The correlations between AVOC or BVOC proxies and selected PMF factors are not sufficient unless specificity is shown. The authors should show the same O₃ x AVOC, ALWC x AVOC, and BVOC-related proxy correlations for all factors. Otherwise, these correlations may simply reflect common diurnal cycles, boundary-layer evolution, or pollution accumulation rather than source-specific formation.

In addition, the number of data points in Fig. S25 is much smaller than expected from the online dataset. The authors should explain how these points were averaged or selected. They should also specify which AVOCs and BVOCs were included in the proxy calculations.

Response: Thank you for this important comment. We agree that correlations with BVOC- and AVOC-related proxies, when presented only for selected PMF factors, are insufficient to demonstrate source specificity. These relationships may also be influenced by common diurnal variations, boundary-layer evolution, meteorological covariation, and pollution accumulation. We have therefore expanded the proxy analysis and revised its interpretation accordingly.

Following the reviewer's suggestion, the relationships with $O_3 \times BVOC$, $O_3 \times AVOC$, $O_3 \times NO_2 \times BVOC$, and $ALWC \times AVOC$ are now presented for all seven PMF factors in Fig. S28. This cross-factor comparison allows the relative specificity of these relationships to be evaluated across the complete PMF solution. The correlations are now used only to characterize the atmospheric conditions associated with the enhancement of each factor and are not treated as independent evidence for assigning a unique biogenic or anthropogenic source.

We have also clarified the construction of the VOC proxies. The BVOC concentration was defined as the sum of the measured C_5H_8 and $C_{10}H_{16}$ concentrations, whereas the AVOC concentration was defined as the sum of the measured C_6H_6 , C_7H_8 , C_8H_{10} , and C_9H_{12} concentrations. The corresponding proxies were calculated by combining these grouped VOC concentrations with O_3 , NO_2 , or $ALWC$, as indicated. These definitions have now been explicitly added to the revised Supplementary Information and the caption of Fig. S28.

The relatively small number of points in the original Fig. S25 resulted from the temporal averaging procedure rather than from limited availability of online measurements. The correlations were not calculated using all individual high-time-resolution observations. Instead, a fixed factor-specific rising period was identified from the diurnal profile of each factor, and the factor signal and corresponding proxy were averaged over this period for each day. Each point therefore represents one daily mean during the rising period of the relevant factor. This procedure was used to examine factor-proxy covariation specifically during factor enhancement. The averaging procedure and the factor-specific time windows are now explicitly described in the revised Supplementary Information. Nevertheless, we acknowledge that this treatment cannot completely eliminate the influence of boundary-layer evolution or other shared atmospheric variability.

In summary, these proxy correlations are no longer used to label entire PMF factors as biogenic- or anthropogenic-dominated. As described in our response to Comment 1, the factors have been renamed Daytime OOM-1, Daytime OOM-2, Nighttime OOM-1, Nighttime OOM-2, Nighttime OOM-3, Regional Background OOM, and Pollution-Episode OOM. Their interpretations are based on the combined evidence from molecular composition, temporal behavior, atmospheric variables, and air-mass transport. These revisions avoid interpreting potentially nonspecific proxy correlations as definitive evidence of precursor origin.

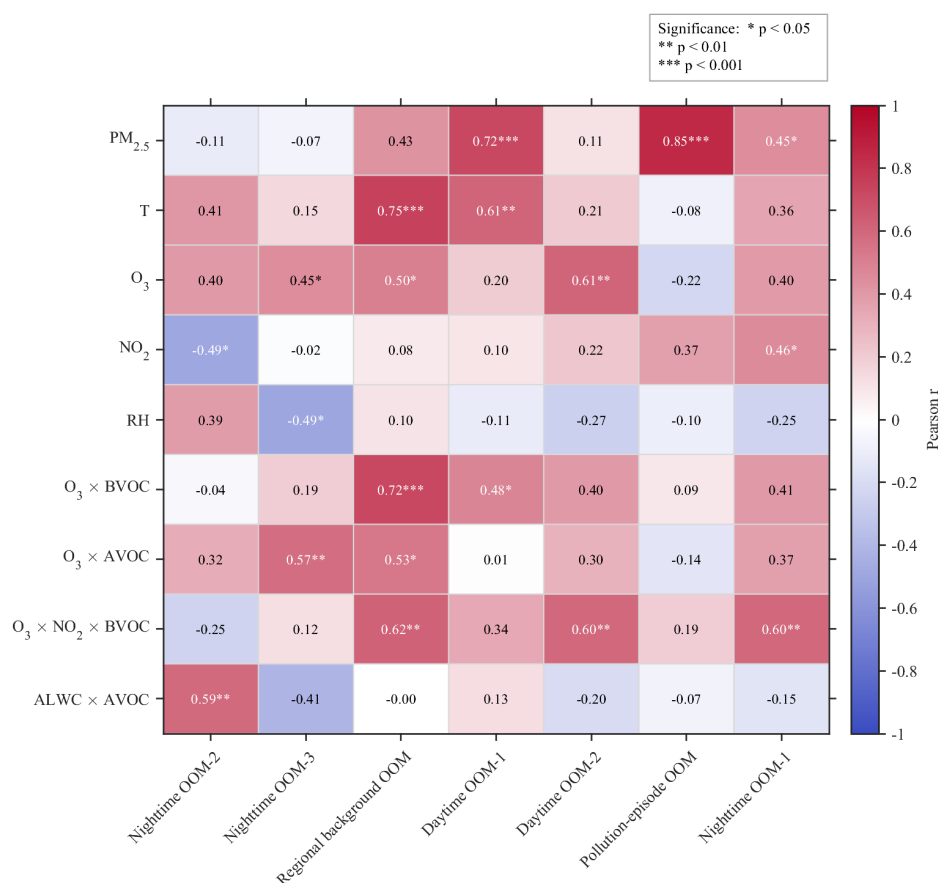


Figure S28. Pearson correlation coefficients between the seven PMF-resolved particle-phase OOM factors and selected atmospheric variables and formation-related proxies. For each factor, a factor-specific rising period was defined from its mean diurnal profile. The factor signal and the corresponding atmospheric variables or proxies were averaged over this period for each day, and the correlations were calculated using these daily means. The variables include PM_{2.5}, temperature (T), O₃, NO₂, relative humidity (RH), O₃ × BVOC, O₃ × AVOC, O₃ × NO₂ × BVOC, and ALWC × AVOC. BVOC was calculated as the sum of the measured C₅H₈ and C₁₀H₁₆ concentrations, whereas AVOC was calculated as the sum of the measured C₆H₆, C₇H₈, C₈H₁₀, and C₉H₁₂ concentrations. Values within the cells represent Pearson correlation coefficients (*r*), with colors indicating their direction and magnitude. Asterisks indicate statistical significance: * $p < 0.05$ (*), ** $p < 0.01$ (**), and *** $p < 0.001$ (***). ALWC denotes aerosol liquid water content.

Reviewer: The VIA was operated at 300 °C, but the manuscript does not sufficiently address whether thermal decomposition or fragmentation affects the observed formulas. This is especially important for organic nitrates, peroxides, oligomers, and thermally labile HOMs. The authors should clarify whether the detected ions mainly represent intact molecules or may include thermal decomposition products.

Response: Thank you for this important comment. We agree that the detected signals may include thermally generated products and cannot universally be assumed to represent intact particle-phase molecules. To evaluate the temperature dependence of the measured molecular composition, we compared the complete assigned OOM spectra obtained from 160 to 300 °C at 20 °C intervals. Pairwise cosine similarities are now presented in Fig. S2a, and a compound-level comparison between the independently normalized spectra at 220 and 300 °C is shown in Fig. S2b. The two normalized spectra yielded a cosine similarity of 0.933, indicating broadly similar overall molecular distributions but also measurable compound-specific changes.

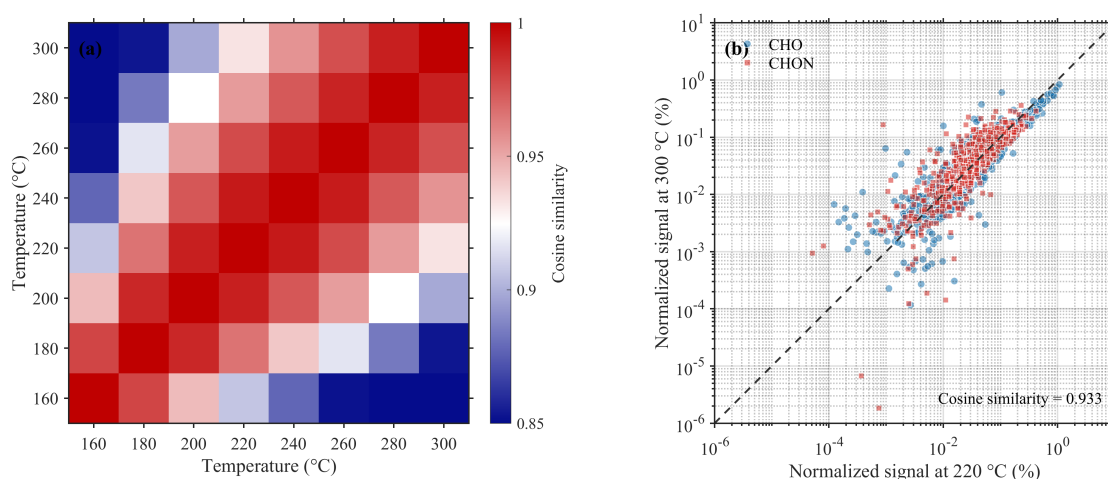


Figure S2. Temperature dependence of the assigned particle-phase OOM composition. (a) Cosine similarity matrix for OOM spectra obtained between 160 and 300 °C at 20 °C intervals. (b) Comparison of the relative signals of individual OOM molecular formulas at 220 and 300 °C. The spectra at each temperature were independently normalized to their respective total assigned OOM signals. Blue circles and red squares represent CHO and CHON compounds, respectively. The dashed line denotes the 1:1 relationship.

We have revised Sect. 2.2.1 (Lines 184-200) and added Sect. S1.5 to present this analysis. The revised manuscript explicitly states that increasing temperature may promote more complete volatilization while also inducing decomposition or transformation of thermally labile compounds, including organic nitrates, peroxides, oligomers, and highly oxygenated compounds. Therefore, the detected formulas may represent a combination of intact volatilized molecules and thermally generated products.

We no longer claim that thermal decomposition is negligible. Instead, 300 °C is described as an empirically selected operating temperature that maximized the assigned OOM signal under the

tested conditions. The possible effects of incomplete volatilization and thermal decomposition on both measured concentrations and molecular distributions are explicitly discussed as methodological uncertainties.

Reviewer: It is not clear how the whole VIA-NO₃-CIMS system was calibrated for particle-phase organic measurements. The manuscript describes a sulfate/sulfuric-acid-based empirical calibration, but this does not fully establish the response of the complete system to organic aerosol, including particle transmission, evaporation efficiency, vapor losses, ionization efficiency, and compound-dependent sensitivity. The authors should clarify what exactly was calibrated, which parts of the system were included, and how the calibration factor should be applied to diverse particle-phase OOMs. The statement that VIA-NO₃-CIMS detects about 22% of AMS-derived SOA should be interpreted with this limitation in mind.

Response: Thank you for your important comment. We agree that the original manuscript did not present the complete calibration procedure clearly enough and did not adequately distinguish the empirical response calibration from an absolute calibration of the entire VIA-NO₃-CIMS system for organic aerosol.

In response to the reviewer's comment, we have substantially expanded Sect. 2.4.2 (Lines 322–380) to present the complete empirical quantification framework. The revised text is reproduced below to clarify the definition, derivation, and application of the empirical system response coefficient:

To obtain semi-quantitative estimates from the VIA-NO₃-CIMS measurements, the detected ion signals were first normalized to the total nitrate reagent-ion signal. The number concentration of each OOM was estimated as:

$$[OOM_i]_{molec} = \ln(1 + \frac{\sum_{n=0}^1 [OOM_i \cdot (HNO_3)_n \cdot NO_3^- + (OOM_i - H)^-]}{\sum_{n=0}^1 [(HNO_3)_n \cdot NO_3^-]}) \cdot \frac{C_i}{\eta_{p,i} \eta_{evap,i} \eta_{v,i}} \quad (4)$$

where the numerator includes the nitrate-adduct channels $OOM_i \cdot (HNO_3)_n \cdot NO_3^-$ ($n = 0$ and 1) and the deprotonated channel $(OOM_i - H)^-$, while the denominator represents the total nitrate reagent-ion signal. Here, C_i is the compound-specific NO₃-CIMS calibration coefficient, $\eta_{p,i}$ is the particle transmission efficiency before evaporation, $\eta_{evap,i}$ is the effective evaporation efficiency, and $\eta_{v,i}$ is the transmission efficiency of the evaporated vapor through the cooling and transfer lines.

For convenience, the compound-specific calibration coefficient and the efficiencies associated with particle transmission, evaporation, and post-evaporation vapor transmission were combined into an effective system response coefficient:

$$C_{sys,i} = \frac{C_i}{\eta_{p,i} \eta_{evap,i} \eta_{v,i}} \quad (5)$$

The individual terms contributing to $C_{sys,i}$ were not independently characterized for each OOM, and compound-specific system response coefficients could therefore not be determined. Instead, $C_{sys,i}$ was approximated using a sulfate-derived empirical system response coefficient, C_{emp} .

This coefficient was derived by comparing the normalized sulfate-derived HSO_4^- signal measured by VIA- NO_3 -CIMS with the particulate sulfate mass concentration independently measured by the AMS. The normalized HSO_4^- signal was strongly correlated with the AMS sulfate concentration ($r=0.88$, Fig. S9a). Linear regression forced through the origin yielded a slope of $5.99 \mu\text{g m}^{-3}$ per normalized signal unit. Conversion of this slope using the molar mass of sulfate gave:

$$C_{emp} = (3.76 \pm 0.05) \times 10^{10} \text{ molecules cm}^{-3}.$$

Because particulate sulfate passed through the VIA inlet, evaporation tube, cooling and transfer lines, and NO_3^- ionization region before detection, C_{emp} represents the aggregate response of the field-configured measurement system to particulate sulfate detected as HSO_4^- . In the present analysis, $C_{sys,i} \approx C_{emp}$ was applied to all detected OOMs. The resulting concentrations should therefore be regarded as semi-quantitative, sulfate-equivalent estimates rather than compound-specifically calibrated concentrations.

The corresponding mass concentration of compound i was calculated using its molecular weight:

$$[\text{OOM}_i]_{\mu\text{g}/\text{m}^3} = [\text{OOM}_i]_{\text{molec}} \times \frac{MW}{N_A} \times 10^{12} \quad (6)$$

where MW is the molecular weight (g mol^{-1}) and N_A is Avogadro's number.

We recognize that applying this sulfate-derived coefficient uniformly to diverse OOMs assumes an equivalent effective response that cannot be verified with the available data. Different organic compounds may exhibit different volatilization, wall-loss, and NO_3^- -ionization sensitivity. The resulting OOM concentrations are therefore now consistently described as semi-quantitative estimates rather than absolute measurements of total particle-phase OOM mass.

Accordingly, we have revised the statement concerning the approximately 22% contribution. The revised manuscript no longer states that VIA- NO_3 -CIMS “detects 22% of SOA.” Instead, it states that the campaign-average semi-quantitative concentration of the OOM components detected by

VIA-NO₃-CIMS corresponded to approximately 22% of AMS-derived SOA. This value should not be interpreted as the absolute recovery efficiency of VIA-NO₃-CIMS or as the actual fraction of all particle-phase OOMs present in SOA.

Other minor comments:

Reviewer: Line 113: The manuscript should clarify what “first” means: first in China, first in eastern China, or first at Nanjing/SORPES. The title, abstract, and conclusions should use a consistent and accurate scope.

Response: We thank the reviewer for pointing out the ambiguity in our use of “first.” In the original manuscript, the placement of “first” alongside the SORPES/Nanjing location could be read as referring either to the first deployment of VIA-NO₃-CIMS anywhere or to a first deployment at that specific site. We have clarified that our intended claim is the first field deployment of VIA-NO₃-CIMS in eastern China. The title, Abstract, Introduction, and Conclusions have been revised to use this same geographical scope.

Reviewer: The VIA setup needs more complete reporting, including the manufacturer/brand or whether it was custom-built. The authors should also state how often the gas denuder was replaced or regenerated, and how denuder breakthrough was checked during the campaign.

Response: We thank the reviewer for this comment. We have expanded Sect. 2.2.1 (Lines 154–161) to clarify that the VIA was custom-built in our laboratory following a previously reported general design, with adaptations for the experimental configuration used in this study.

Multiple regenerable denuders were used in rotation during the campaign. The installed denuder was replaced every three days with a clean or regenerated unit, and the removed unit was regenerated offline before reuse. Denuder breakthrough was not independently quantified using an upstream–downstream gas-phase challenge experiment during the campaign. As shown in Fig. 1, the particle/background switching unit was located upstream of the activated-carbon denuder, so both the ambient-aerosol and HEPA-filtered background streams passed through the same denuder. Subtraction of the immediately preceding HEPA background would therefore be expected to remove much of any gas-phase signal arising from limited breakthrough. These details have been clarified in Sect. 2.2.1 (Lines 169–176).

Reviewer: Line 364: The authors report 1,695 high-confidence OOMs, but it is unclear how many peaks were initially detected, how many were fitted, how many meaningful peaks remained unfitted, and what fraction of the total signal they represented. This information is needed to judge how representative the fitted molecular dataset is.

Response: We thank the reviewer for this comment. We agree that the original manuscript did not

provide sufficient information to evaluate the representativeness of the identified molecular dataset. We have therefore added a signal-weighted comparison of the identified OOM features and unidentified peaks as Fig. S16 and reported the corresponding result in Sect. 3.2.1 (Lines423-425).

The 1,695 identified OOM features accounted for 87.5% of the total background-corrected positive ion signal within the analyzed mass range, whereas the remaining unidentified peaks accounted for 12.5%. We now clarify that the reported molecular distributions characterize the identified fraction of the VIA-NO₃-CIMS signal rather than the complete detected particle-phase signal.

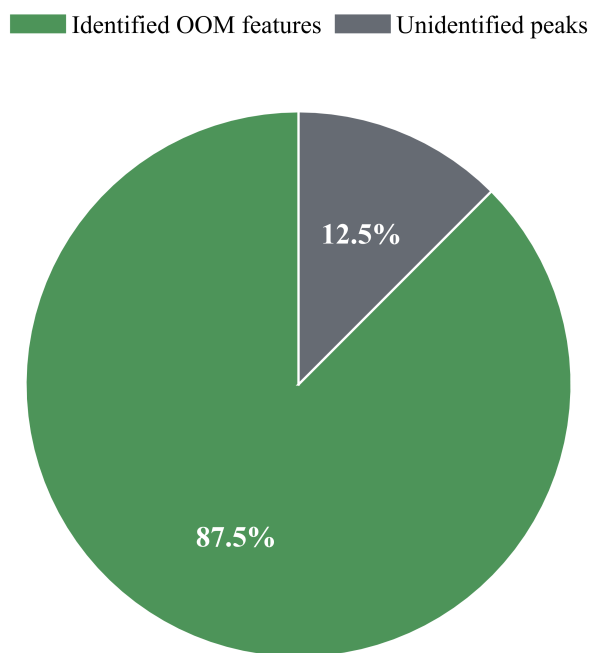


Figure S16. Signal-weighted fractions of identified OOM features and unidentified peaks in the VIA-NO₃-CIMS dataset. The 1,695 identified OOM features accounted for 87.5% of the total background-corrected positive integrated signal within the analyzed mass range, while the remaining unidentified peaks accounted for 12.5%.