Anonymous Referee #1

General comments:

This paper presents results from a novel offline AMS methodology, expanding on existing techniques, making offline AMS analyses more feasible on a larger scale. The study offers a thorough characterization of the ultrasonic atomization system employed and an impressive comparison to real-time AMS analysis of ambient PM. A notable advantage of the offline AMS methodology proposed here is the ability to more easily fold into existing PM sampling networks. This makes it a particularly attractive work to labs and organizations looking to improve our understanding of PM chemistry on a global scale. The manuscript is clear and well written. I have largely only minor questions/needs for clarification. Once these concerns are resolved, I recommend publication in AMT.

Reply: We thank the referee for affirming the significance and robustness of this work. We appreciate the referee's constructive comments, which have helped improve the clarity and quality of the manuscript. We have carefully addressed each comment in detail below, with our responses to each comment shown in blue and revisions to the manuscript shown in green. All line numbers refer to the revised manuscript (without tracked changes) unless explicitly stated.

Specific comments:

Line 408-409: Were the blanks filter blanks, or was filtered air sampled by the real-time AMS (or both)?

Reply: The blanks referred to here are filtered air measurements for the real-time AMS, obtained by periodically inserting a high-efficiency particulate air (HEPA) filter upstream of the cyclone for approximately 30 minutes. During these periods, the co-located SPARTAN stations also sampled filtered air, with the corresponding filter sampling durations adjusted accordingly. In addition, field filter blanks for the offline measurements were collected separately following the standard SPARTAN sampling protocol, with one blank filter included in each eight-filter cartridge and exposed without air being drawn through it. We have clarified the distinction between online AMS background measurements and offline field blank filters in the revised manuscript.

Lines 414-416: "In total, six paired cartridges were sampled, yielding a collection of 42 paired filter samples, along with six paired field blank filters collected without air being drawn through them."

Lines 422-424: "Background measurements for the online AMS were obtained by periodically inserting a high-efficiency particulate air (HEPA) filter upstream of the cyclone during the campaign."

Figure 3: Does the OOA fraction represent the fraction of total NR-PM mass? E.g. fraction of OOA = OOA/total NR-PM? Or is this a fraction of just the organic portion of the sample? This is not clear from the main text or figure caption.

Reply: The OOA fraction represents the fraction of OA that is oxygenated, calculated as OOA/OA, rather than the fraction of total NR-PM mass. We have clarified this definition in the figure color bar title, figure caption, and the corresponding text throughout the revised manuscript and Supplement, where applicable.

Lines 456-458: "Points are colored by the fraction of oxygenated OA (OOA) in OA, determined from positive matrix factorization (PMF) of the online measurements."

Figure S4/organic formula assignments: From the main text, it seems like the organic ion family assignments are based on the HR-AMS/PIKA ion assignments although this is not fully clear. Was the FTIR analysis used here as well? The differentiation between saturated and unsaturated hydrocarbons (ions) is not terribly convincing based on AMS data alone given the additional fragmentation induced by the vaporizer. To the author's credit, however, the data provided does make chemical sense with that differentiation in mind.

Reply: The organic ion family assignments are based only on the HR-AMS spectra and are not informed by the FT-IR measurements. We agree that distinguishing saturated and unsaturated hydrocarbons using AMS data alone is subject to uncertainty due to fragmentation. Accordingly, we have combined saturated and unsaturated hydrocarbon ions into a single hydrocarbon ion family (C_xH_y) throughout the analysis and revised the corresponding text and Figure S4. This revision does not affect our conclusion that the hydrocarbon ion family exhibits lower recovery than the oxygenated ion families.

Lines 470-477: "To better understand compositional differences, OA recovery is further examined by grouping high-resolution AMS fragment ions into representative chemical families (Daellenbach et al., 2016). Fragments are classified into mono-oxygenated ions ($CHO_{z=1}$), poly-oxygenated ions ($CHO_{z>1}$), and hydrocarbon ions (C_xH_y). Recovery varies substantially across these ion families (Figure S4), with the highest recovery (mean ± standard deviation) observed for the $CHO_{z>1}$ family (80 ± 35 %), followed by the $CHO_{z=1}$ family (48 ± 21 %), while the hydrocarbon ion family shows the lowest recovery (32 ± 18 %)."

Supplement Lines 276-283: "

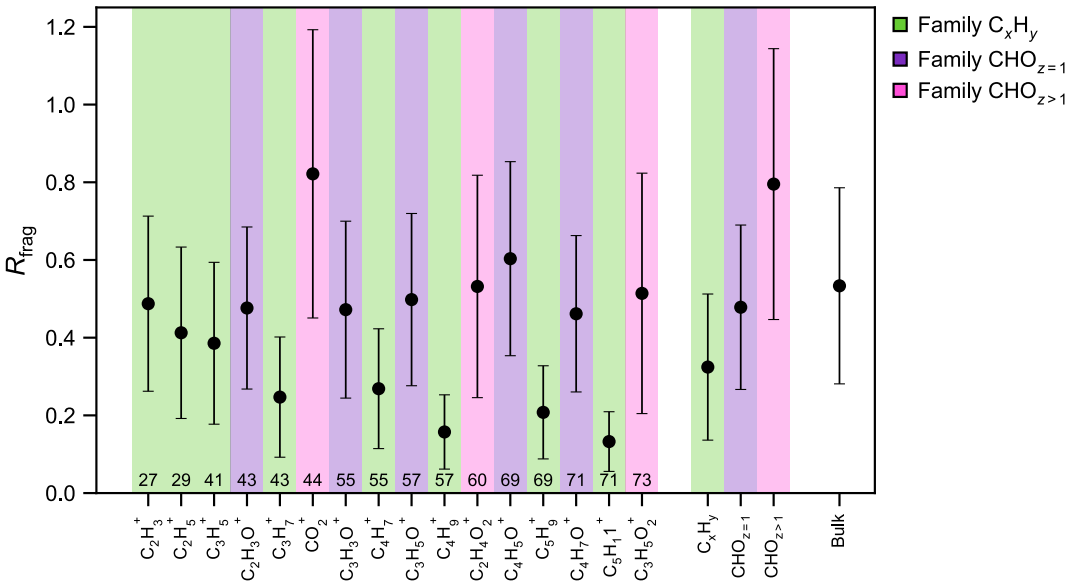

Figure S4. Recovery (mean ± standard deviation) of individual organic fragments and chemical families for samples collected in St. Louis. Recovery (R_{frag}) is calculated as the ratio of offline concentrations to the corresponding online measurements, with a value of 1 indicating 100 % recovery. Fragments are color-coded by family, including mono-oxygenated ions ($CHO_{z=1}$), poly-oxygenated ions ($CHO_{z>1}$), and hydrocarbon ions (C_xH_y). Inserted numbers indicate the nominal mass of each fragment. Families include all respective fragments weighted by their mass contribution."

Line 473/PMF analysis: I would like to see a more thorough explanation of the PMF analysis, specifically why the two factor solution was chosen. From the reviewer's perspective, there is an overreliance on the chemical interpretability factor (from mass spectral features alone) for this solution, which is not often the limiting factor in a PMF analysis. The Q/Qexp vs P plot is atypical, as is the choice of factor solution with the highest Q/Qexp. Neither of those are exclusionary as-is, but certainly they warrant a more thorough discussion as to why this was deemed the appropriate solution. For example, a time series analysis for tracer ions for OOA/HOA factor profiles including any correlations with external events (e.g. traffic patterns) would help to support this PMF solution and factor assignments.

Reply: We thank the referee for this suggestion. We have substantially expanded the PMF discussion by clarifying the objective of PMF analysis, providing a more comprehensive evaluation of PMF diagnostics, and validating the selected factors through temporal comparisons with characteristic tracer ions and secondary inorganic species.

In this study, PMF is applied to the online AMS dataset to derive representative OA factor profiles for evaluating the offline AMS methodology, rather than to perform detailed source apportionment for the St. Louis measurement period. Because the framework is intended for future application

across diverse SPARTAN sites, we prioritize a solution that resolves the dominant OA components expected across a wide range of environments and is diagnostically robust.

We evaluate the PMF solutions using PMF diagnostics, factor interpretability, and comparisons with higher-order solutions. The selected two-factor solution resolves the two dominant OA components, OOA and HOA, with factor profiles consistent with established AMS spectral characteristics. The reconstructed OA closely reproduces the measured OA time series, with residuals centered near zero and without systematic temporal or mass spectral structure. Varying the FPEAK parameter produces only minor changes in factor contributions and profiles, suggesting low rotational ambiguity and stable factor profiles. An FPEAK value of 0 is selected because it produces the lowest $Q/Q_{expected}$ among the tested rotations. Although higher-order solutions produce lower $Q/Q_{expected}$ values, they primarily introduce site-specific components or exhibit factor splitting, rather than resolving additional broadly interpretable OA components (Figure S7). The three-factor solution resolves an additional factor with enhanced m/z 60 ($C_2H_4O_2^+$) and m/z 73 ($C_3H_5O_2^+$), indicating a potential biomass burning OA (BBOA)-influenced component. While resolving this factor provides additional source information specific to the St. Louis measurement period, biomass burning contributions are site- and season-dependent, and including a BBOA-influenced factor would introduce complexity without improving general applicability. Moreover, applying the three-factor solution to the offline AMS measurements does not change the conclusions of this study. Solutions with four or more factors primarily exhibit factor splitting rather than resolving additional physically meaningful components. Therefore, we select the two-factor solution as the most appropriate framework for this study.

To further support the selected solution, we compare the diel profiles of resolved factors with characteristic tracer ions and secondary inorganic species (Figure S8). Although sampling was conducted at an urban background site away from major primary emission sources, the resolved HOA factor shows clear diel variability, with weak enhancement after sunrise, an afternoon minimum, and a more pronounced increase during late evening, which collectively reflect locally influenced semivolatile material and ubiquitous diel patterns in boundary layer height and temperature (Li et al., 2023, 2025). In contrast, OOA exhibits a relatively stable diel profile, consistent with its predominantly regional and secondary nature, and afternoon photochemical production that offsets mixed layer growth. Relationships between OOA and inorganic species are stronger for sulfate, which is also more oxidized and regional. In addition, HOA is correlated with its characteristic ion fragments, m/z 41 ($C_3H_5^+$), m/z 55 ($C_4H_7^+$), and m/z 69 ($C_5H_9^+$) (r^2 = 0.81, 0.87, and 0.90, respectively), while OOA is correlated with m/z 44 (CO_2^+) (r^2 = 0.75).

Accordingly, we substantially expand the PMF discussion by adding a new section, Text S3. PMF analysis of online AMS measurements, to the revised Supplement (Supplement Lines 65-114). The complete text is provided verbatim in Text S3 and is not repeated here to avoid redundancy. We also add Figure S7, which summarizes alternative PMF solutions, and Figure S8, which compares

the temporal behavior of resolved factors with characteristic tracer ions and secondary inorganic species.

References:

Li, Y., Martin, R.V., Li, C., Boys, B.L., van Donkelaar, A., Meng, J., and Pierce, J.R.: Development and evaluation of processes affecting simulation of diel fine particulate matter variation in the GEOS-Chem model, Atmos. Chem. Phys., 23, 12525–12543, 2023.

Li, Y., Martin, R.V., Zhang, Y., Zhang, D., van Donkelaar, A., Zhu, H., and Meng, J.: Interpreting measurements of the global diurnal variation of fine particulate matter using the GEOS-Chem model, Environ. Sci. Technol. Air, 2, 1575–1585, 2025.

Lines 492-502: “OOA and HOA are the two most prevalent OA factors resolved in a wide range of environments. Although they can be further resolved into subtypes such as less-oxidized OOA, more-oxidized OOA, and isoprene-derived OA, the occurrence and relative contributions of these subtypes vary across locations, making them difficult to resolve consistently across the globally distributed SPARTAN sites. Therefore, we select this two-factor solution to support the objective of deriving representative OA factor profiles for evaluating the offline AMS methodology and facilitating its future application throughout SPARTAN. We further evaluate the selected solution using PMF diagnostics, factor interpretability, and comparisons of temporal variations in factor contributions with characteristic tracer ions and secondary inorganic species (Text S3; Figures S6–S8).”

Supplement Lines 297-300: “

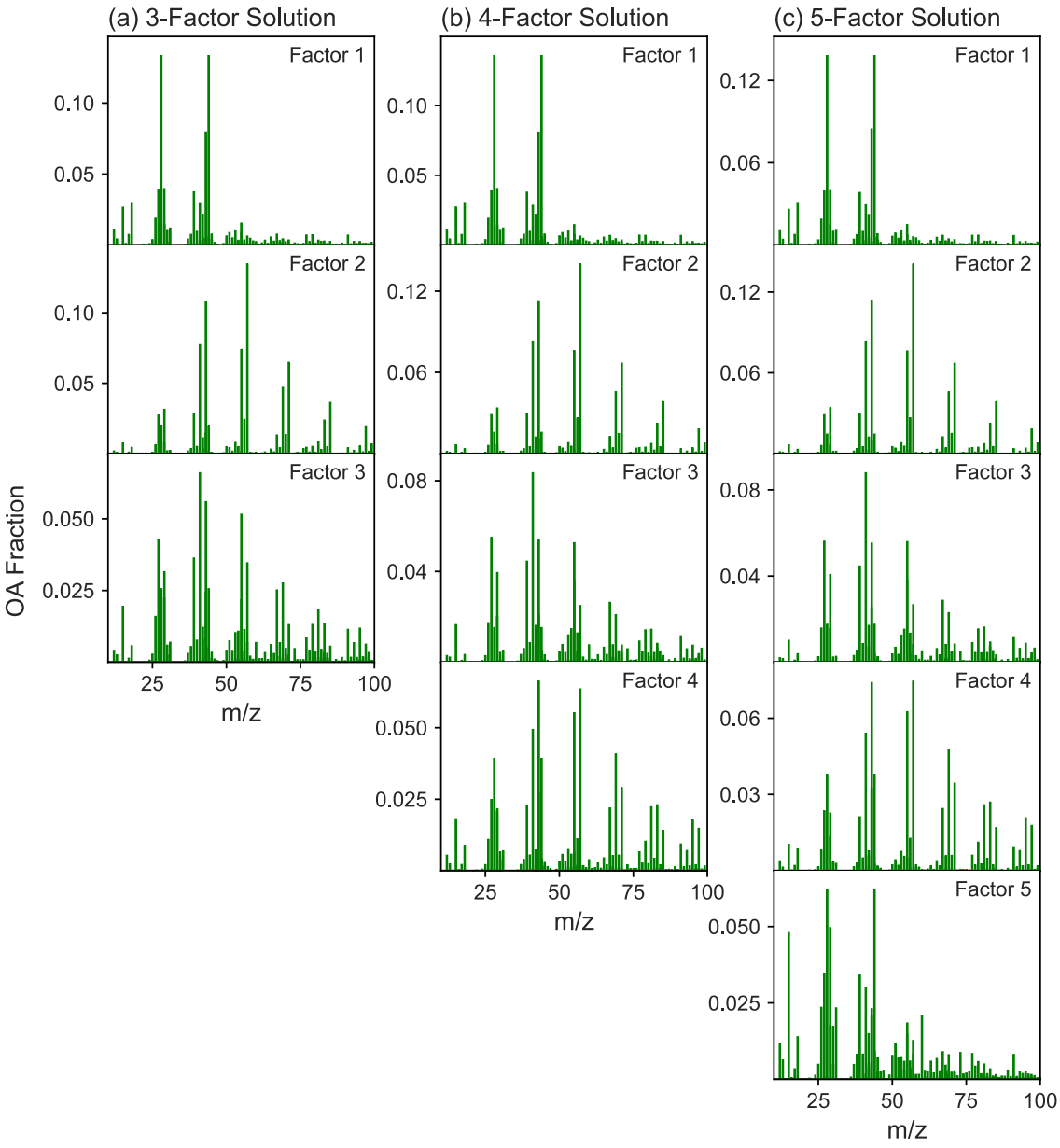

Figure S7. Factor profiles from additional positive matrix factorization (PMF) solutions applied to online AMS measurements in St. Louis, including (a) three-factor, (b) four-factor, and (c) five-factor solutions."

Supplement Lines 301-312: "

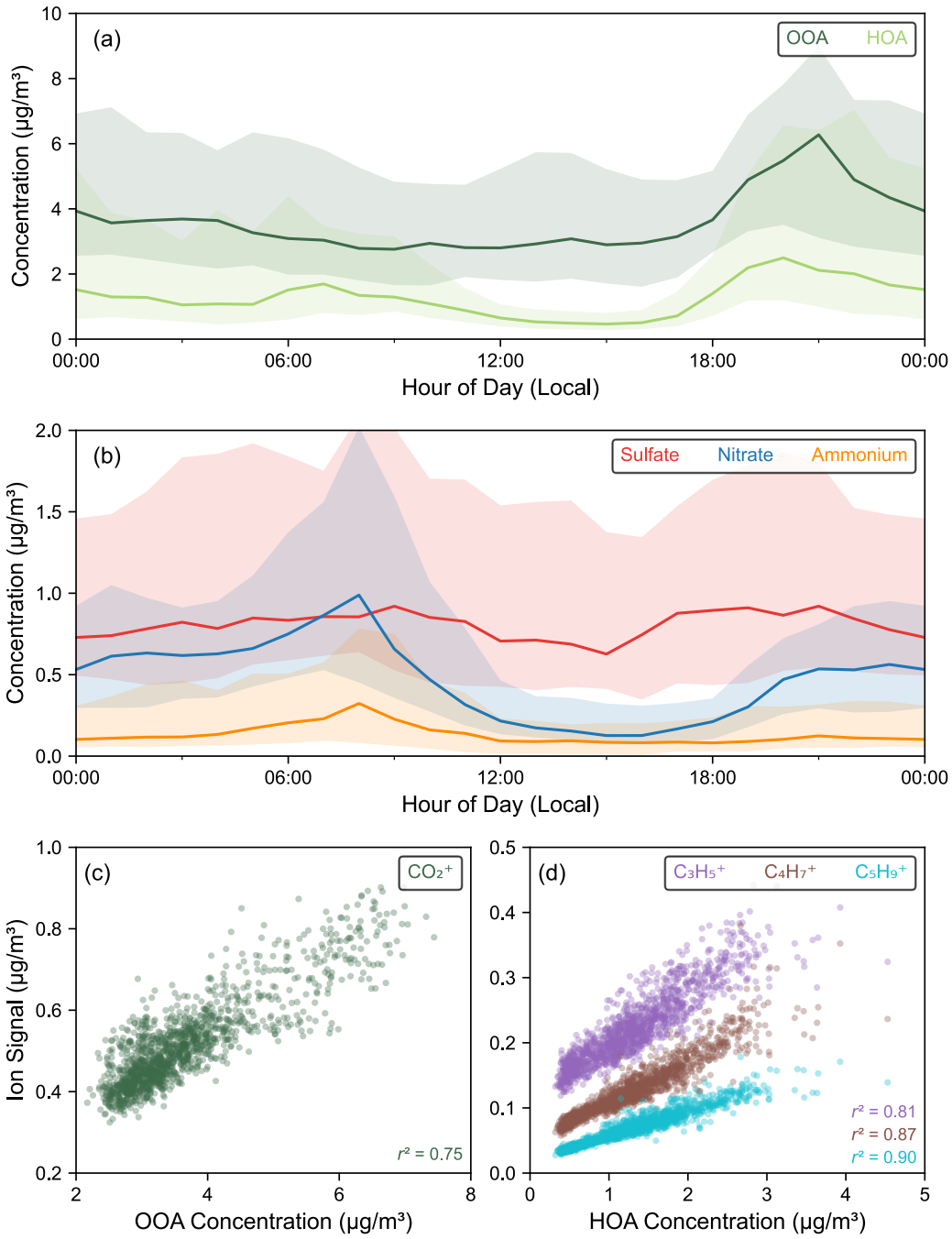

Figure S8. Diel variations of species measured by the online AMS in St. Louis, including (a) oxygenated OA (OOA) and hydrocarbon-like OA (HOA) resolved by positive matrix factorization (PMF), and (b) inorganic species, including sulfate, nitrate, and ammonium. Lines represent median values over the measurement period, and shaded areas indicate the interquartile range (25th–75th percentile). OOA and HOA are shown in dark and light green, respectively, while sulfate, nitrate, and ammonium are shown in red, blue, and orange, respectively. The x-axis represents the local hour of day. Comparisons of OA factors with their characteristic ion fragments

are shown for (c) OOA with m/z 44 (CO_2^+), and (d) HOA with m/z 41 ($C_3H_5^+$), m/z 55 ($C_4H_7^+$), and m/z 69 ($C_5H_9^+$). Scatter plots are based on median per-minute-of-day values over the measurement period. Annotations indicate the coefficient of determination (r^2)."

Figure 7: The generally strong agreement between the reconstructed and online OA mass concentration is impressive. For the extreme outlier samples (e.g. with ratios closer to 2 or 0.5), I would be interested to see if there are any outstanding chemical features of those samples that might offer some rationale for the determined high/low reconstructed mass.

Reply: We appreciate the referee's suggestion. We examine samples with large deviations between reconstructed and online OA concentrations to determine whether they share any distinctive chemical characteristics. Specifically, we investigate their relationship with OOA and HOA recoveries, online and offline OOA and HOA fractions, OA concentrations, sulfate concentrations, and the organic-to-sulfate ratio in the extract.

We find that the reconstructed-to-online OA ratio is primarily associated with variability in OOA recovery (r^2 = 0.95, Figure S13a). Because reconstructed OA is calculated using the mean OOA recovery, samples with OOA recoveries higher than the mean recovery are systematically overestimated, whereas samples with OOA recoveries lower than the mean recovery are systematically underestimated. Thus, deviations of sample-specific OOA recovery from the representative recovery used in the reconstruction directly propagate into the reconstructed-to-online OA ratio. In particular, the sample with a reconstructed-to-online OA ratio greater than 2 exhibits an OOA recovery exceeding unity, likely reflecting uncertainty in recovery estimation, whereas samples with reconstructed-to-online OA ratios below 0.5 exhibit low OOA recoveries. In contrast, HOA recovery shows a weaker relationship with the reconstructed-to-online OA ratio (r^2 = 0.79, Figure S13d), as HOA represents a relatively small fraction of the total OA in these samples. We do not identify any other chemical characteristics that consistently distinguish these outlier samples from the remainder of the dataset. These results indicate that variability in factor recovery is an important source of uncertainty in the OA reconstruction. Accordingly, we add this discussion to the revised manuscript.

Lines 580-591: "We further examine samples with large deviations between reconstructed and online OA concentrations to identify potential drivers of reconstruction uncertainty (Figure S13). Samples with OOA recoveries higher (or lower) than the mean recovery used in the reconstruction generally correspond to overestimation (or underestimation) of reconstructed OA, respectively. In contrast, HOA recovery shows a weaker association with reconstructed OA due to its relatively small contribution to total OA in these samples. No other chemical characteristics, including online and offline OOA and HOA fractions, OA concentrations, sulfate concentrations, and the organic-to-sulfate ratio in the extract, are found to consistently distinguish these samples from the remaining dataset. The uncertainty associated with variability in factor recovery is further discussed in Section 3.4."

Supplement Lines 361-375: “

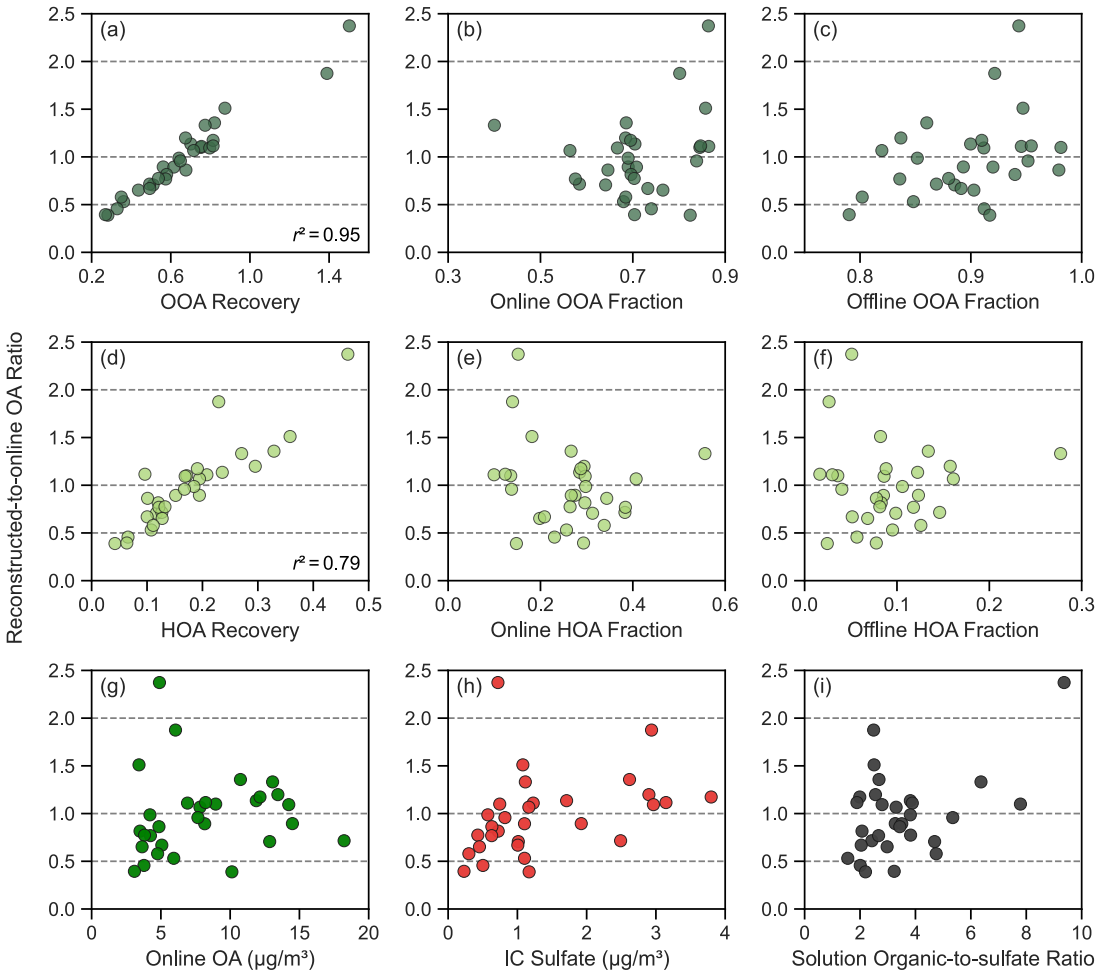

Figure S13. Comparison of the reconstructed-to-online OA ratio with factors influencing offline OA reconstruction: (a) oxygenated OA (OOA) recovery, (b) online OOA fraction in OA, (c) offline OOA fraction in OA, (d) hydrocarbon-like OA (HOA) recovery, (e) online HOA fraction in OA, (f) offline HOA fraction in OA, (g) online OA concentration, (h) IC-measured sulfate concentration, and (i) solution organic-to-sulfate ratio. Markers related to OOA and HOA are shown in dark green (a–c) and light green (d–f), respectively. Green, red, and dark gray markers represent OA concentration, sulfate concentration, and organic-to-sulfate ratio in panels (g–i), respectively. Reconstructed OA concentrations are calculated by dividing each offline-derived factor by its mean recovery. Offline factor contributions are obtained using constrained positive matrix factorization (PMF), with the HOA factor profile constrained to the corresponding online PMF profile (*a*-value = 0.1). Dashed horizontal lines indicate reconstructed-to-online OA ratios of 0.5, 1.0, and 2.0. The coefficient of determination (r^2) is shown for the relationship between the reconstructed-to-online OA ratio and OOA recovery (a) and HOA recovery (d).”

Lines 567-569: The purpose of equating IC-measured sulfate with offline AMS-measured sulfate is not clear and is rather confusing from a reader's perspective. They two measurements of sulfate are certainly "intrinsically linked" as they are coming from the same source, but the two instruments are not equivalent. They measure sulfate in completely different ways and have distinct strengths and limitations (some of which are mentioned in the main text). This is true even with online AMS measurements of sulfate. Showing the correlation of IC-measured and offline AMS-measured sulfate would be critical here, but that comparison is not shown. There are no chemical or instrumental reasons to assume those two measurement schemes would provide identical results. There is plenty of published work showing that online and offline AMS should correlate well with IC measurements, but none that suggest they are equivalent in any way.

As an example of the confusion introduced here, in Figure S8a, the y-axis is labeled "IC (offline AMS) sulfate ($\mu g/m^3$)". Are those measurements from the IC analysis or from the offline AMS analysis? The units imply it is offline AMS-derived measurements, although one could arrive at those units from a typical IC analysis and the quantification method outlined in section 3.2. The comparison of online AMS-sulfate to both offline AMS-sulfate and IC-sulfate is of interest, and it's not clear what is being offered here.

Beyond that, it is not clear what is gained by equating those two measurements as done in Figure S8. Either this equivalency needs to be further explained in the main text (likely with the addition of the IC-measured and offline-AMS measured sulfate comparison if possible) or the language used should be reworked to avoid this confusion altogether.

Reply: We thank the referee for identifying this potential source of confusion. We agree that our original wording was unclear and should not equate IC-measured sulfate with offline-AMS measured sulfate. These are fundamentally different measurements and serve distinct roles in the offline AMS methodology. Specifically, this study includes three distinct sulfate measurements: (1) online AMS directly measures sulfate in ambient aerosol, (2) IC measures sulfate in filter extracts and is used to determine ambient sulfate concentration in the offline methodology, and (3) offline AMS measures sulfate in regenerated particles following nebulization of the filter extract.

Because IC sulfate represents the ambient sulfate concentration, comparing IC sulfate with online AMS sulfate is more appropriate and provides an additional evaluation of the consistency between online and offline measurements beyond OA. We have therefore revised the y-axis label in Figure S15a (formerly Figure S8a) to "IC sulfate ($\mu g/m^3$)" and updated the figure caption accordingly. The original label was ambiguous because the y-axis represents IC sulfate rather than offline AMS sulfate. The reported unit of $\mu g/m^3$ is obtained by converting the IC sulfate concentration ($\mu g/mL$) using the extract volume (mL) and the corresponding air sampling volume (m^3).

We further clarify that ambient sulfate concentrations are determined from IC measurements, whereas offline AMS sulfate serves only as the internal standard under the assumption that the organic-to-sulfate ratio is preserved during aerosol regeneration. Ambient OA concentrations are

therefore calculated by multiplying the AMS-derived organic-to-sulfate ratio by the IC-measured ambient sulfate concentration. The same approach is applied to ammonium and nitrate. Accordingly, we have revised the manuscript throughout to distinguish the roles of the three sulfate measurements.

Lines 316-318: "Ambient OA concentration is subsequently obtained by multiplying this AMS-derived organic-to-sulfate ratio by an independently quantified IS concentration."

Lines 386-389: "Note that the offline OA concentrations discussed throughout this study refer to OA concentrations calculated through Eq. 5, rather than raw OA signals directly reported by the offline AMS."

Lines 615-618: "We find strong agreement among online AMS measurements of sulfate in ambient aerosol, IC measurements of sulfate in water extracts, and XRF measurements of sulfur in aerosol collected on filter samples, with r^2 of 0.80 and 0.95 for the respective comparisons (Figures S15a and S15b)."

Supplement Lines 391-398: "Panel (a) compares online AMS sulfate concentrations with sulfate concentrations measured by Ion chromatography (IC), and panel (b) compares IC-measured sulfate (expressed as S) with sulfur measured by X-ray fluorescence (XRF). Panels (c) and (e) compare offline AMS-derived ammonium and nitrate with online AMS measurements, respectively, while panels (d) and (f) compare offline AMS-derived ammonium and nitrate with concentrations measured by IC. Offline AMS-derived ammonium and nitrate are quantified using sulfate as the internal standard, assuming a calibration slope of unity. This internal standard quantification approach is not applicable to sulfate."