Anonymous Referee #2

Ren et al. present a filter-based offline AMS framework to characterize OA chemically and use those fingerprints for source apportionment. Such analyses are becoming more popular, thus this study is timely. Especially, extending current analytical frameworks relying on Quartz Fiber filters to Teflon filters is valuable - as networks typically only use one or the other. After addressing the following points, I recommend the study for publication.

Reply: We thank the referee for the positive assessment and for affirming the significance 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.

Overall, I have two concerns regarding the presented results:

1. I agree with the authors that future studies will not have collocated online AMS/ACSM data available, especially given the scope to apply the method to a global scale. I am afraid that the presented source apportionment data flow in the main body of the results would almost never happen like the one presented here: 1. fully constraining all factor profiles with an online AMS PMF is unrealistic, 2. PMF would likely be used instead of another NNMF implementation. I appreciate the sensitivity tests that the authors present, but would wish for including more details on those results at least in the SI (e.g. factor time series comparisons with e.g. BClf and secondary inorganic aerosol as well as recoveries obtained for each test). In addition, it is crucial to also perform an additional test that follows best practices of constrained source apportionment analyses (e.g. Canonaco, 2021, https://amt.copernicus.org/articles/14/923/2021/), i.e. only to constrain primary OA compnenents with literature spectra - in your case HOA (not OOA). In my personal opinion, these latter results would likely be the best fit to be presented in the main body of source apportionment comparisons.

Reply: We thank the referee for this constructive comment. In response, we have clarified the applicability of the proposed methodology, substantially revised the offline factor analysis workflow by presenting the HOA-only constrained PMF solution as the primary analysis, and substantially expanded the PMF evaluation.

The objective of factor analysis in this study is to estimate ambient OA from offline OA measurements. Specifically, offline OA is first separated into offline OOA and HOA, two major OA components commonly observed in ambient aerosol. Ambient OOA and HOA concentrations are then estimated by correcting their corresponding offline concentrations using factor-specific recoveries. In this methodological evaluation, representative OOA and HOA factor profiles derived from co-located online AMS measurements are used as reference profiles. We agree that future applications will generally not have co-located online AMS measurements available. To address this point, we additionally evaluate the workflow using complementary factor profiles from the

literature. Although the use of literature profiles introduces additional uncertainty, the reconstructed OA remains in generally good agreement with online AMS observations (Figure S16). These results demonstrate that the proposed workflow remains applicable without co-located factor profiles, while acknowledging that the choice of reference factor profiles remains an important source of uncertainty (Section 3.4). Accordingly, we revise the manuscript as follows:

Lines 653-668: "In the reconstruction workflow described above (Figure 7), we use reference factor profiles derived from co-located online AMS measurements as prior information in the offline factor analysis. However, such site-specific, highly accurate factor profiles may not be available at many SPARTAN locations with limited online AMS observations. For future applications, representative OOA and HOA factor profiles from the literature can instead be used as a priori constraints in the offline factor analysis. To evaluate this approach, we use the AMS Spectral Database to identify four additional pairs of deconvoluted OOA and HOA factor profiles (Ulbrich et al., 2009a, 2009b, 2009c). These profiles are derived from studies conducted in the US (Zhang et al., 2005), Zurich (Lanz et al., 2008), China (Elser et al., 2016), and an average across five sites (Ng et al., 2011), representing variability in OOA and HOA spectral characteristics. Each pair of OOA and HOA profiles is applied to the St. Louis offline OA measurements using weighted NNLS regression. Weighted NNLS is used for this sensitivity analysis because it provides a simple framework for evaluating multiple sets of fixed factor profiles while remaining conceptually consistent with the fully constrained PMF approach."

In the workflow, offline factor analysis requires assumptions regarding the extent to which OOA and HOA mass spectra measured from offline filters represent those in ambient air. Following the referee's recommendation, we systematically examine four PMF configurations with different levels of constraint on the similarity between offline and online factor profiles:

1. Unconstrained PMF. This configuration assumes that factors are resolved directly from offline OA mass spectra without any prior information from online measurements. Neither the OOA nor HOA profile is constrained.
2. OOA-only constrained PMF. This configuration assumes that the OOA factor profile is preserved during offline analysis and can therefore be represented by the online OOA profile, whereas the HOA profile may differ and is allowed to vary freely.
3. HOA-only constrained PMF. This configuration assumes that the HOA factor profile is preserved during offline analysis and can therefore be represented by the online HOA profile, whereas the OOA profile is allowed to adapt to the offline measurements. Consistent with the referee's recommendation and conventional constrained PMF practice (Canonaco et al., 2021), we test both a fully fixed HOA profile (a-value = 0) and partially constrained HOA profiles (a-values = 0.1, 0.3, and 0.5).
4. Constrained OOA-and-HOA PMF. This configuration assumes that both OOA and HOA factor profiles are preserved during offline analysis. We test both fully constrained (a-value = 0) and partially constrained (a-values = 0.1, 0.3, and 0.5) solutions. The fully constrained

case is conceptually similar to the weighted non-negative least-squares (NNLS) regression used in the original manuscript, although the optimization methods differ.

The unconstrained and OOA-only constrained solutions do not resolve a physically interpretable HOA factor, likely because the offline method preferentially recovers the more water-soluble OOA fraction. In contrast, both HOA-only constrained and constrained OOA-and-HOA configurations successfully resolve physically interpretable OOA and HOA factors (Figure S9). Across these successful solutions, estimated factor contributions, recoveries, and reconstructed OA concentrations are generally consistent (Figures S11 and S12). Mean OOA recovery ranges from 58 % to 67 %, while mean HOA recovery ranges from 9.9 % to 24 %. After applying the corresponding factor-specific recoveries, reconstructed OA agrees with online OA, with regression slopes ranging from 0.94 to 1.1 and normalized mean biases (NMBs) ranging from −0.68 % to 5.2 %. These results indicate that the primary findings of this study, including the substantially higher recovery of OOA than HOA and the improvement in reconstructed OA after applying factor-specific recoveries, are robust across constrained PMF configurations.

We agree with the referee that the HOA-only constrained configuration provides the most appropriate primary analysis because it reliably resolves both OOA and HOA while minimizing assumptions about the offline factor profiles. By partially constraining only the less abundant HOA, which cannot be resolved reliably by unconstrained PMF, this approach allows the OOA profile to adapt to the measured offline spectra. In contrast, constraining both OOA and HOA, either through constrained PMF or through the weighted NNLS regression used in the original manuscript, requires the stronger assumption that both factor profiles are preserved during offline analysis, which poses challenges for future applications across diverse SPARTAN sites. Among the tested HOA-only solutions, we select the solution with an a-value = 0.1 as the primary analysis. This solution provides satisfactory PMF diagnostics (Figure S10), physically interpretable factor profiles (Figure S9b), and good agreement between reconstructed and online OA, with the lowest NMB (0.012 %; Figure S12b). We recognize that other partially constrained HOA solutions may also be appropriate, and their close agreement with the selected solution supports the robustness of the analysis.

Accordingly, we substantially revise the manuscript to present the HOA-only constrained PMF solution with an a-value of 0.1 as the primary approach for offline factor analysis. Other constrained PMF configurations and the original weighted NNLS analysis are now presented as sensitivity tests. Specifically, we add a new section, Text S4. Constrained PMF analysis of offline AMS measurements, to the revised Supplement (Supplement Lines 116-183). The complete text is provided verbatim in Text S4 and is not repeated in this response. We also include PMF diagnostics for the selected solution (Figure S10) and comparisons of factor profiles, recoveries, and reconstructed OA across alternative constrained configurations (Figures S9, S11, and S12). Corresponding figures and discussion have also been revised throughout the manuscript and Supplement, including Figures 5–7 and the original Figure S7 (now Figure S14), where appropriate.

These revisions do not change the main conclusions but provide a more systematic and methodologically rigorous evaluation of the offline factor analysis and OA reconstruction.

Reference:

Canonaco, F., Tobler, A., Chen, G., Sosedova, Y., Slowik, J.G., Bozzetti, C., Daellenbach, K.R., El Haddad, I., Crippa, M., Huang, R.-J., Furger, M., Baltensperger, U., and Prevot, A.S.H.: A new method for long-term source apportionment with time-dependent factor profiles and uncertainty assessment using SoFi Pro: Application to 1 year of organic aerosol data, Atmos. Meas. Tech., 14, 923–943, 2021.

Lines 245-249: "PMF analyses are performed using the PMF Evaluation Toolkit (PET) v3.08E or the multilinear engine (ME-2) (Paatero, 1999) implemented through the Source Finder (SoFi Pro 6.4; Datalystica Ltd., Villigen, Switzerland) (Canonaco et al., 2013). Details of the PMF analysis are provided in the Supplement."

Lines 503-523: "We also perform PMF analysis on offline measurements, with the online-derived factor profiles used as a priori constraints in selected configurations. We evaluate four approaches, representing different assumptions about how OOA and HOA factor profiles vary between the online and offline measurements: (1) unconstrained PMF, assuming both factors are resolved directly from the offline OA mass spectra; (2) OOA-only constrained PMF, assuming the online OOA profile is preserved during offline analysis while the HOA profile is allowed to vary; (3) HOA-only constrained PMF, assuming the HOA profile is preserved while the OOA profile is allowed to vary; and (4) simultaneously constrained OOA and HOA PMF, assuming both factor profiles are preserved during offline analysis. The detailed implementation and corresponding results for each approach are described in Text S4. Among the evaluated configurations, the HOA-only constrained configuration with an *a*-value of 0.1 is selected as the primary offline factor analysis approach. The resulting solution resolves physically interpretable OOA and HOA factors (Figure S9b), exhibits satisfactory PMF diagnostics (Figure S10), and yields the lowest normalized mean bias (NMB) among the tested configurations while following conventional constrained source-apportionment practice (Bozzetti et al., 2016, 2017a; Canonaco et al., 2021; Vlachou et al., 2018). As a complementary analysis, offline factor concentrations are also quantified using weighted non-negative least-squares (NNLS) regression against fixed online OOA and HOA factor profiles, providing a simple framework for the sensitivity analyses using literature factor profiles (Text S5)."

Lines 524-531: "Figure 5 compares online and offline concentrations for OOA and HOA. OOA exhibits relatively high recovery (mean ± standard deviation) of 66 ± 27 % and a median of 64 % (50 % and 77 % for the first and third quartiles, respectively). In contrast, HOA recovery is substantially lower, with a mean and standard deviation of 17 ± 9.4 % and a median of 16 % (11 % and 20 % for the first and third quartiles, respectively). Sensitivity tests using additional constrained offline PMF configurations and weighted NNLS regression yield generally consistent

results, with mean OOA recovery ranging from 58 % to 67 % and mean HOA recovery ranging from 9.9 % to 24 % (Figure S11)."

Lines 578-580: "This comparison shows an r^2 of 0.67, a slope of 0.98, and an NMB of 0.012 %. Sensitivity tests using additional constrained offline PMF configurations and weighted NNLS regression yield broadly consistent results (Figure S12)."

Lines 591-592: "When evaluated over longer timescales such as at the cartridge level of one week, agreement improves further, with r^2 increasing to 0.79 (Figure S14)."

Supplement Lines 313-320: "

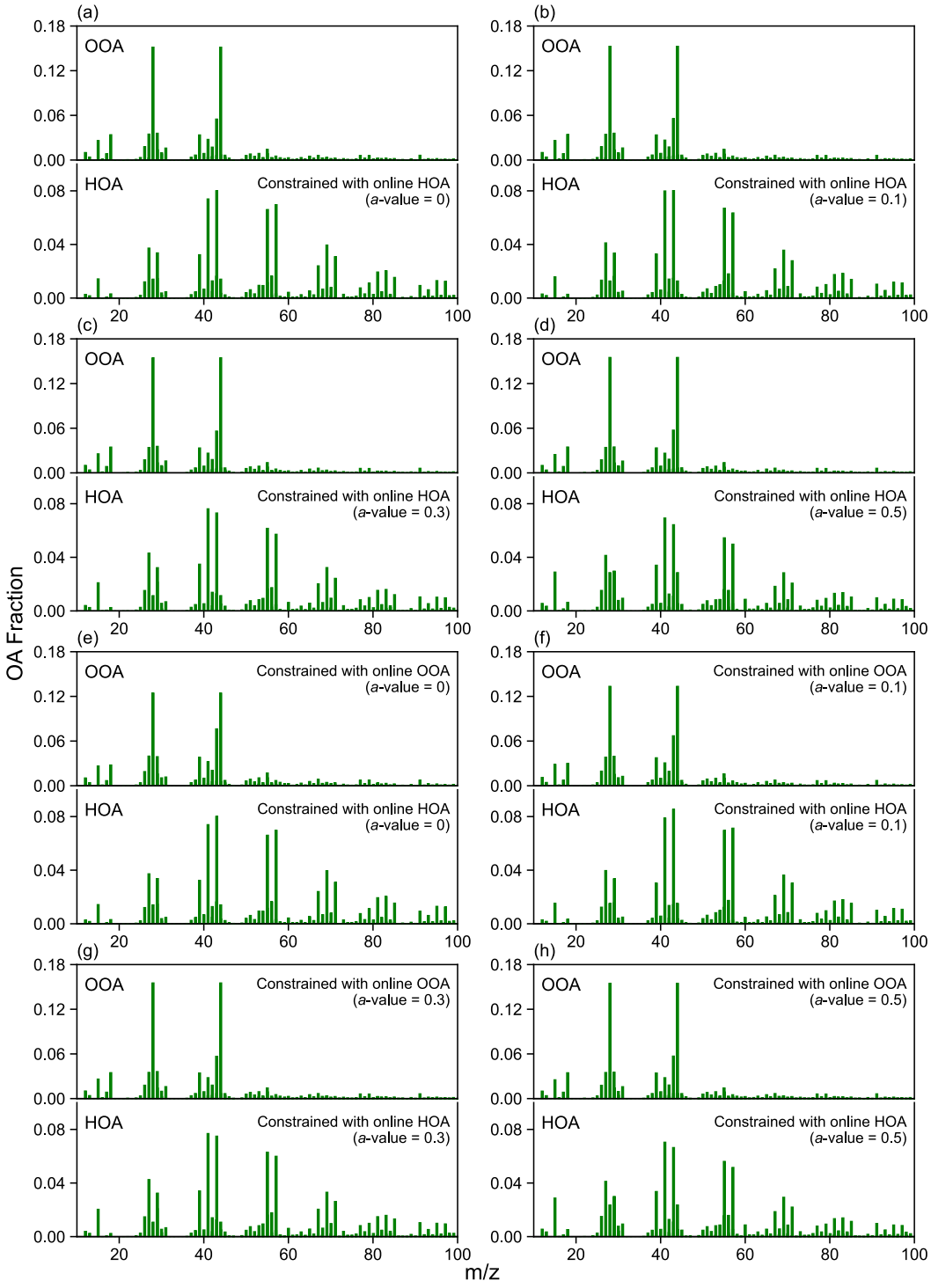

Figure S9. Oxygenated OA (OOA) and hydrocarbon-like OA (HOA) factor profiles resolved by constrained positive matrix factorization (PMF) with the multilinear engine (ME-2) applied to offline AMS data collected in St. Louis. Panels (a–d) show results with only HOA constrained using the corresponding online HOA factor profile with *a*-values of 0, 0.1, 0.3, and 0.5, respectively.

Panels (e–h) show results with both OOA and HOA constrained using the corresponding online OOA and HOA factor profiles with *a*-values of 0, 0.1, 0.3, and 0.5, respectively."

Supplement Lines 321-328: "

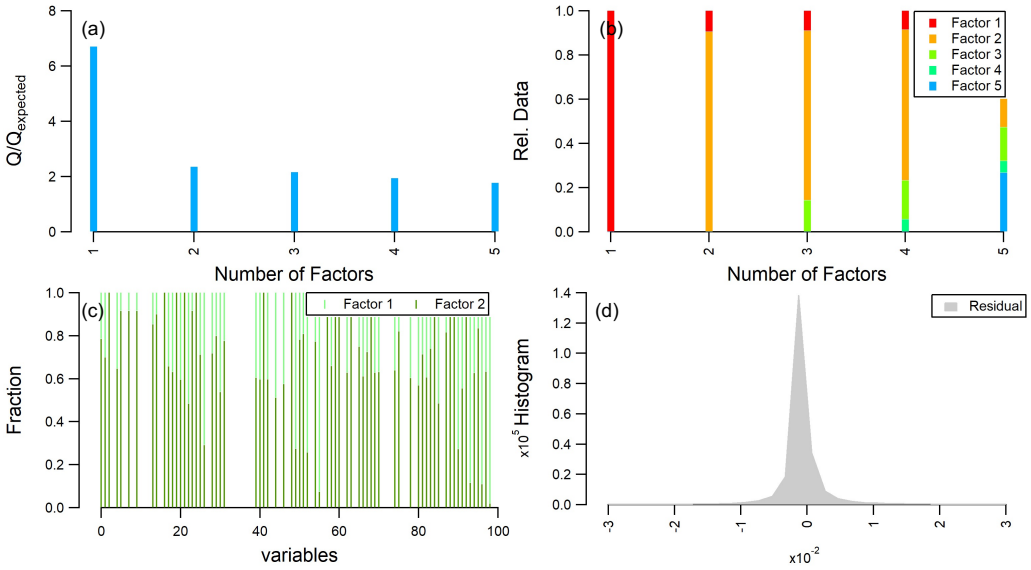

Figure S10. Summary of key diagnostic plots for the constrained positive matrix factorization (PMF) analysis of offline AMS measurements collected in St. Louis using the multilinear engine (ME-2), in which only HOA is constrained using the corresponding online HOA factor profile (*a*-value = 0.1). (a) $Q/Q_{expected}$ as a function of the number of factors, (b) relative contribution of each factor to the explained signal as a function of the number of factors, (c) mass fractions of individual ions for the selected two-factor solution, and (d) distribution of total residuals for the selected two-factor solution."

Supplement Lines 329-342: "

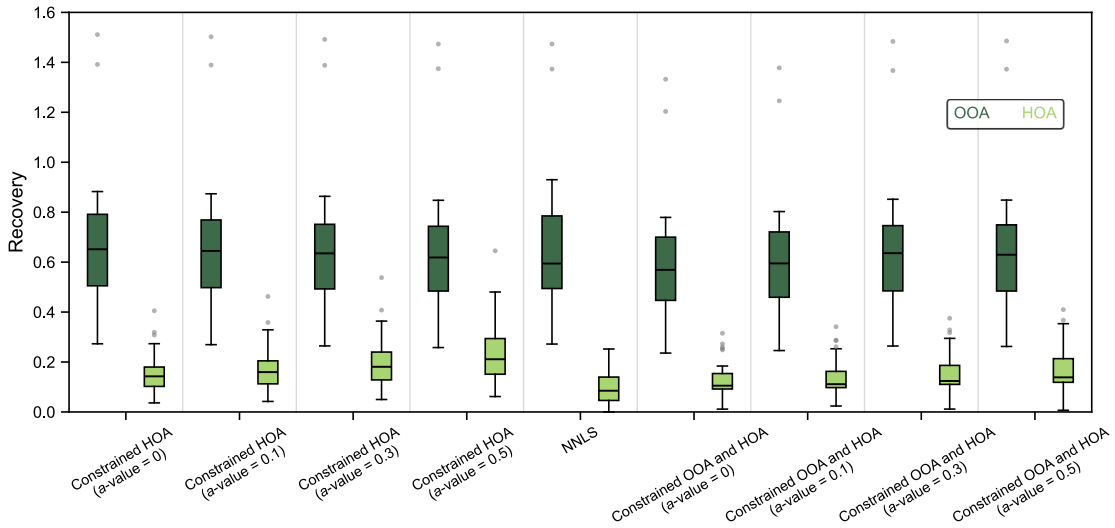

Figure S11. Summary of per-sample oxygenated OA (OOA) and hydrocarbon-like OA (HOA) factor recoveries from constrained positive matrix factorization (PMF) using the multilinear engine (ME-2) and weighted non-negative least-squares (NNLS) regression for offline AMS measurements collected in St. Louis. Panels (a–d) show constrained PMF solutions in which only HOA is constrained using the corresponding online HOA factor profile with *a*-values of 0, 0.1, 0.3, and 0.5, respectively. Panel (e) shows weighted NNLS regression using the fixed online OOA and HOA factor profiles. Panels (f–i) show constrained PMF solutions in which both OOA and HOA are constrained using the corresponding online OOA and HOA factor profiles with *a*-values of 0, 0.1, 0.3, and 0.5, respectively. Dark green boxes represent OOA recoveries, and light green boxes represent HOA recoveries. Boxes indicate the interquartile range (25th–75th percentile) with the median shown as a horizontal line. Whiskers extend to the most extreme values within 1.5× the interquartile range, and gray circles denote extreme values beyond the whiskers."

Supplement Lines 343-360: "

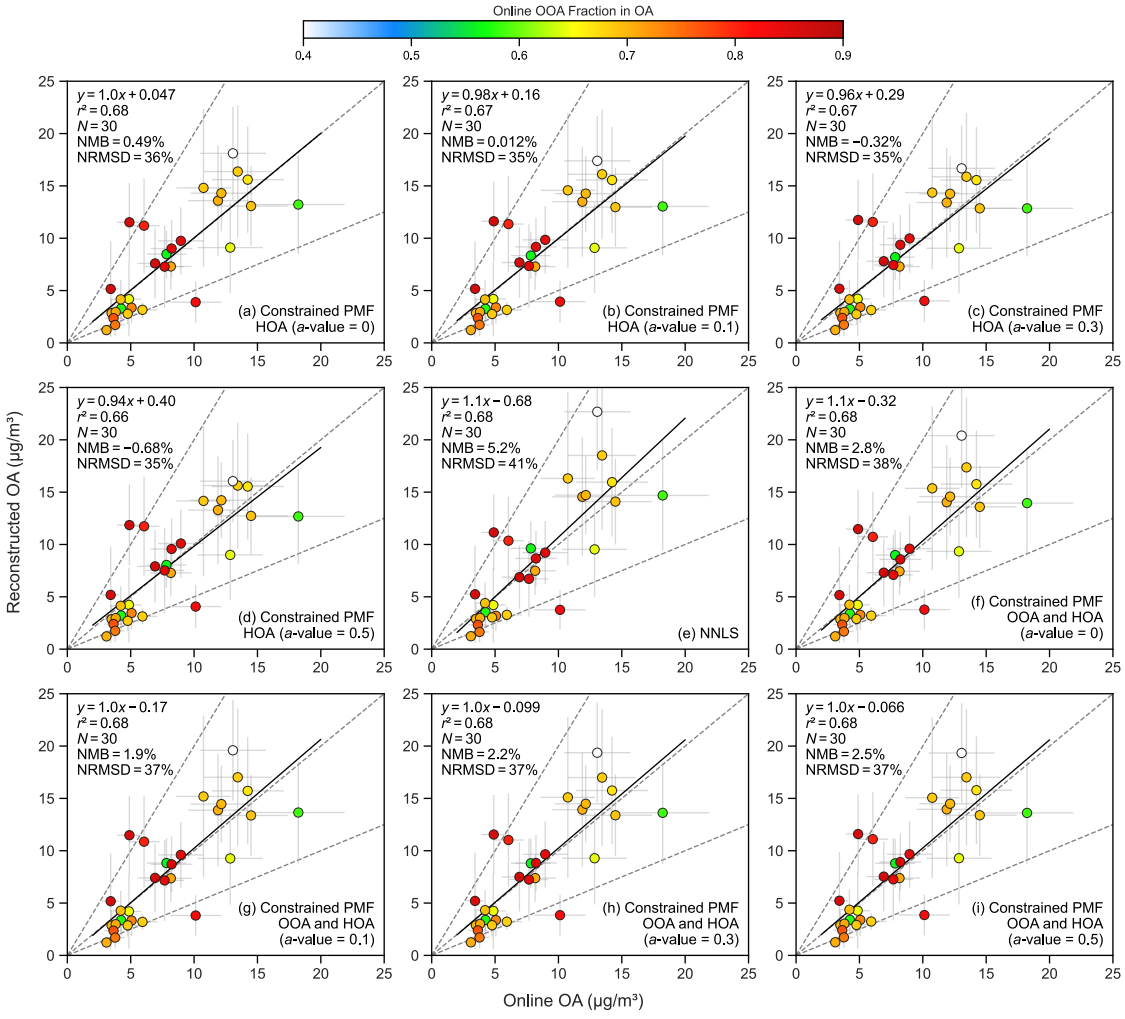

Figure S12. Comparison of reconstructed and online OA concentrations for samples collected in St. Louis. Reconstructed OA concentrations are calculated by dividing each offline-derived oxygenated OA (OOA) and hydrocarbon-like OA (HOA) factor by its mean recovery. Offline factor contributions are determined using (a–d) constrained positive matrix factorization (PMF) with the multilinear engine (ME-2), in which only HOA is constrained using the corresponding online HOA factor profile with *a*-values of 0, 0.1, 0.3, and 0.5, respectively; (e) weighted non-negative least-squares (NNLS) regression with fixed online OOA and HOA factor profiles; and (f–i) constrained PMF using ME-2, in which both OOA and HOA are constrained using the corresponding online OOA and HOA factor profiles with *a*-values of 0, 0.1, 0.3, and 0.5, respectively. Online OA represents the time-averaged concentration over each corresponding filter sampling interval. Horizontal bars indicate the estimated AMS measurement uncertainty of online OA concentrations, while vertical bars indicate the propagated uncertainty of offline OA concentrations. Each point represents the mean across 8 to 12 runs. Points are colored by the fraction of OOA in OA, determined from the PMF of the online measurements. Annotations indicate the ordinary least-squares fit (*y*), coefficient of determination (r^2), number of comparison points (*N*), normalized mean bias (NMB), and normalized root mean square deviation (NRMSD). Dashed lines indicate reference lines with slopes of 0.5, 1, and 2."

In addition, we substantially expand the discussions of both the online and offline PMF analyses in the revised Supplement.

For the online PMF analysis, we add 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. These additional analyses further support the selected two-factor solution. Specifically, measurements were conducted on a third-floor rooftop located away from major primary emission sources to represent an urban background environment. Despite this, the resolved HOA factor exhibits 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). We acknowledge that additional measurements such as BC and NOx would provide further source-specific validation. However, these measurements are not available for the complete study period and therefore could not be included

in the evaluation. This scope is also consistent with the primary purpose of the study, which is to evaluate the offline AMS methodology intended for globally distributed filter measurements rather than to perform a comprehensive source-apportionment analysis for St. Louis.

For the offline PMF analysis, we now present PMF diagnostics for the selected configuration (Figure S10), as well as factor profiles (Figure S9), sample-specific factor recoveries (Figure S11), and reconstructed OA results (Figure S12) for each successful sensitivity case. Temporal analysis of the offline PMF factors and correlation with tracer ions and species is not presented because each offline filter integrates a 24-h sampling period, whereas the offline AMS analysis consists of 8–12 repeated analytical runs of the same extract. These repeated measurements characterize analytical variability rather than temporal variability in ambient aerosol composition.

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: “

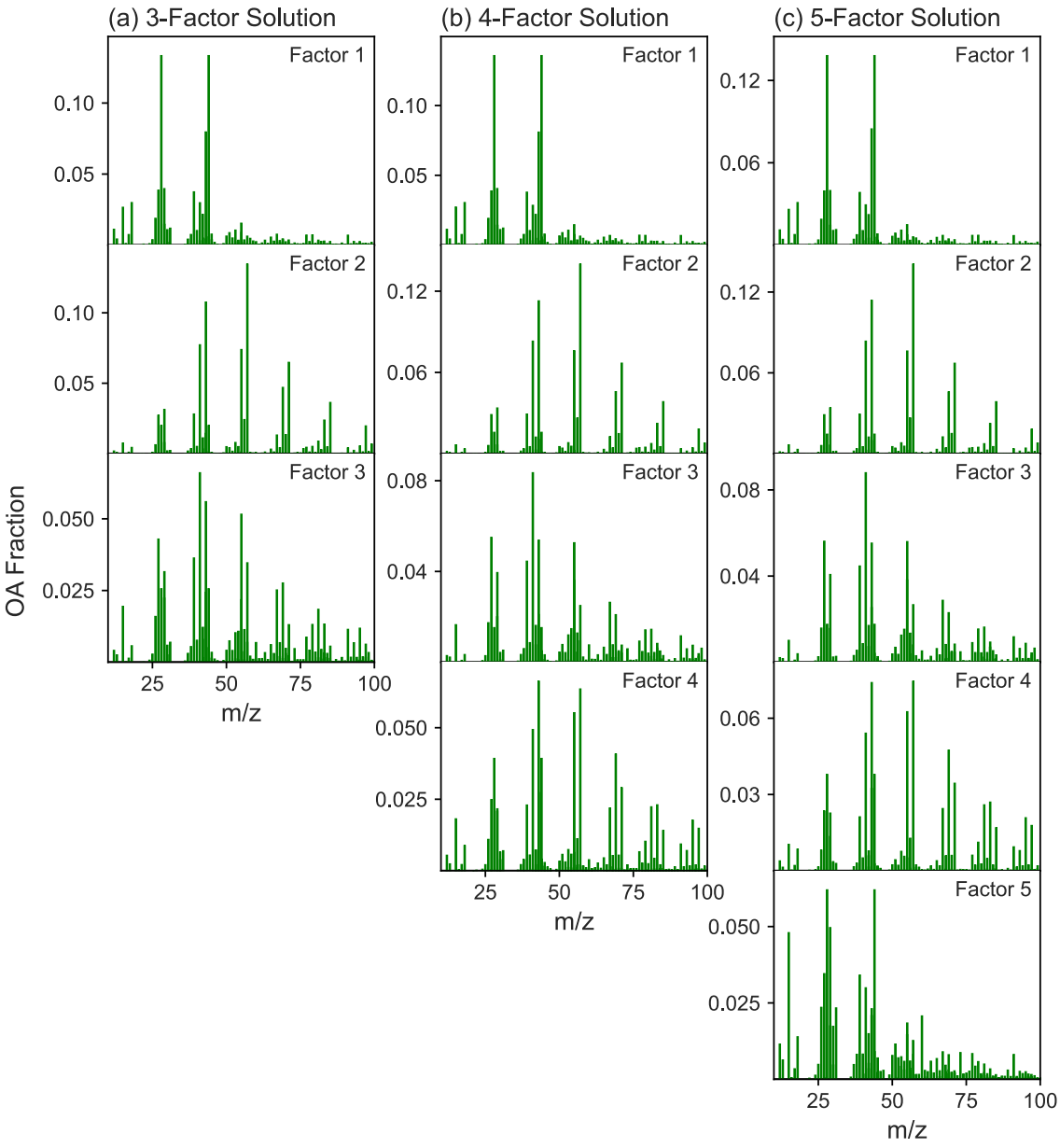

Figure S7. Factor profiles from additional positive matrix factorization (PMF) solutions applied to online AMS measurements in St. Louis, including (a) three-factor, (b) four-factor, and (c) five-factor solutions."

Supplement Lines 301-312: "

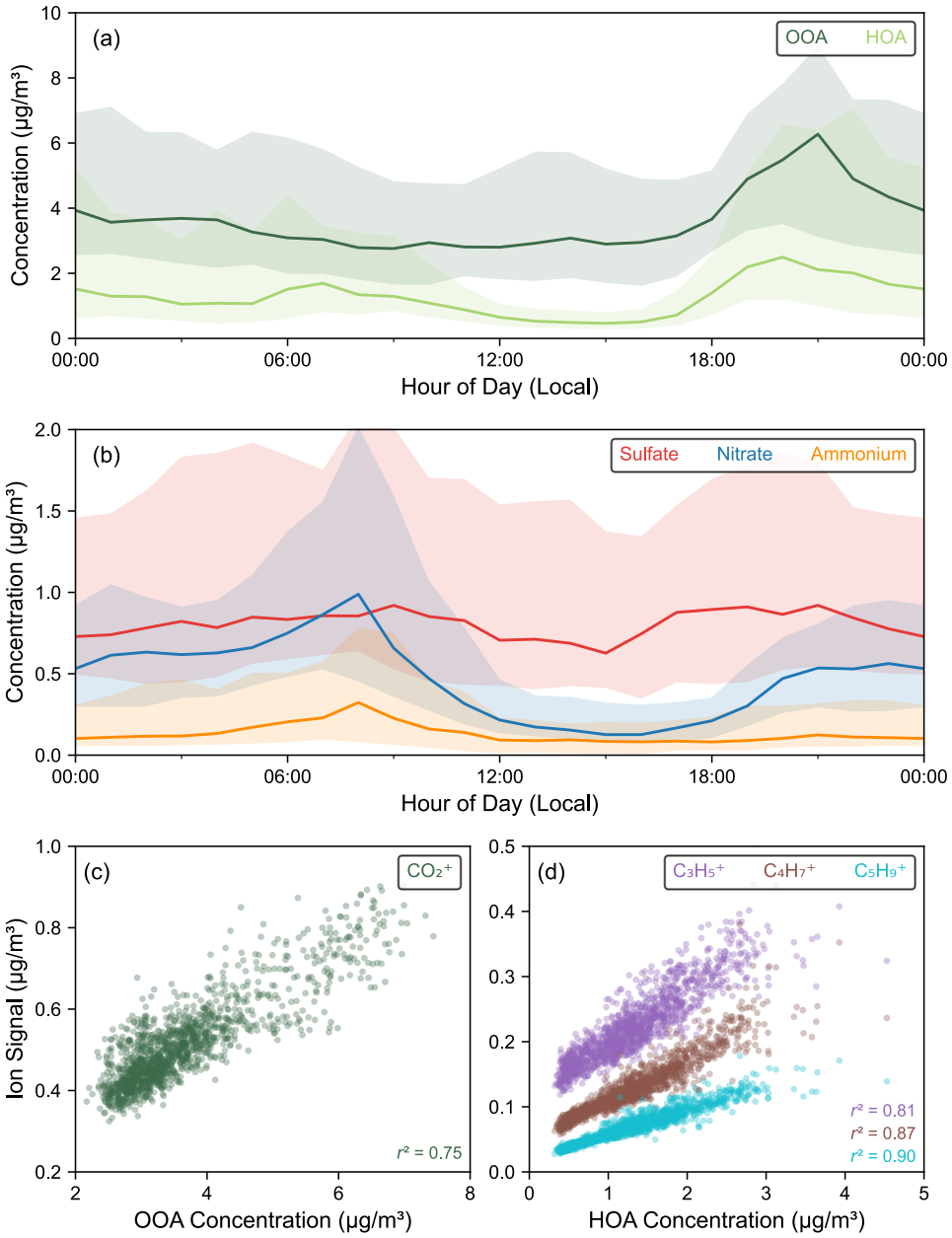

Figure S8. Diel variations of species measured by the online AMS in St. Louis, including (a) oxygenated OA (OOA) and hydrocarbon-like OA (HOA) resolved by positive matrix factorization (PMF), and (b) inorganic species, including sulfate, nitrate, and ammonium. Lines represent median values over the measurement 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)."

2. The authors rely on SO4 for internal standard-based quantification. However, SO4 forms readily refractory salts. Thus, other studies use NO3 as internal standard (isotopically labelled or not), despite the potential evaporative losses of NO3. This should be explored here too, since the approach is intended to be used globally, thus dusty regions too. Further validation of OA, based on the same fraction (i.e. soluble fraction) with a reference method (e.g. TOC analyzer) would be highly recommended to further strengthen the quantification power of the approach.

Reply: We thank the referee for highlighting the selection of internal standard and additional validation of offline OA quantification. We address these concerns as follows:

1. Potential impacts from refractory sulfate salts can be assessed through the complementary XRF and IC comparisons. We select sulfate as the internal standard because it is consistently present in samples, predominantly water-soluble and non-refractory for major atmospheric sulfate species, nonvolatile, and independently quantified by offline AMS, IC, and XRF (through sulfur). We agree that refractory sulfate salts (e.g., $CaSO_4$), particularly in dusty regions, may introduce additional uncertainty by affecting extraction and AMS vaporization. To evaluate this potential limitation, we compare XRF measurements of total sulfur from collected particles with IC measurements of water-soluble sulfate from filter extracts. Samples with substantial contributions from refractory sulfate salts would be expected to show lower IC-derived sulfur relative to XRF-measured sulfur. Therefore, this comparison provides a means to identify samples where sulfate speciation may introduce additional uncertainty.
2. Ambient nitrate is less suitable as an internal standard for SPARTAN applications due to potential organic nitrate interference. Nitrate, including isotopically labeled nitrate, has been successfully used as an internal standard in previous offline AMS studies, primarily through the addition of an external nitrate standard to the extract before nebulization. However, the goal of this study is to develop an offline method that can be seamlessly integrated into SPARTAN by prioritizing internal standards from species already present in the collected aerosol. Using ambient nitrate as an internal standard presents several challenges for SPARTAN applications. First, IC quantifies inorganic nitrate, whereas AMS nitrate signals can include contributions from organonitrates, introducing potential bias. Although a similar consideration applies to sulfate and organosulfates, previous studies have shown that organosulfates typically represent a smaller fraction of total sulfate than organonitrates contribute to total nitrate (Chen et al., 2019; Liao et al., 2015). In addition, nitrate concentrations are more variable and generally lower across SPARTAN sites. Therefore, sulfate provides a more robust internal standard for globally distributed SPARTAN samples.

3. Future comparison with FT-IR measurements will provide independent validation of the OA quantification. We appreciate this suggestion and agree that comparison with an independent reference method would further strengthen validation of the offline OA quantification. We achieve this objective by comparing offline AMS-derived OA with co-located online AMS measurements in this study and will further evaluate the method by comparing offline AMS-derived OA with OA derived from Fourier transform infrared spectroscopy (FT-IR) across SPARTAN sites. TOC analysis of the filter extracts would also provide useful information. However, it is not compatible with the current extraction protocol because the extraction solvent contains methanol (0.2 mL methanol in 6 mL total solution), which would interfere with TOC measurements.

Accordingly, we revise the manuscript to explicitly discuss the potential influence of refractory sulfate salts, the consideration of selecting nitrate as an alternative internal standard, and the opportunity for additional OA validation using complementary measurements.

References:

Chen, Y., Xu, L., Humphry, T., Hettiyadura, A.P.S., Ovadnevaite, J., Huang, S., Poulain, L., Schroder, J.C., Campuzano-Jost, P., Jimenez, J.L., Herrmann, H., O'Dowd, C., Stone, E.A., and Ng, N.L.: Response of the aerodyne aerosol mass spectrometer to inorganic sulfates and organosulfur compounds: Applications in field and laboratory measurements, Environ. Sci. Technol., 53, 5176–5186, 2019.

Liao, J., Froyd, K.D., Murphy, D.M., Keutsch, F.N., Yu, G., Wennberg, P.O., St. Clair, J.M., Crounse, J.D., Wisthaler, A., Mikoviny, T., Jimenez, J.L., Campuzano-Jost, P., Day, D.A., Hu, W., Ryerson, T.B., Pollack, I.B., Peischl, J., Anderson, B.E., Ziemba, L.D., Blake, D.R., Meinardi, S., and Diskin, G.: Airborne measurements of organosulfates over the continental U.S., J. Geophys. Res.-Atmos., 120, 2990−3005, 2015.

Lines 324-328: "In this study, we select sulfate as the internal standard because it is consistently present in samples, predominantly water-soluble and non-refractory for major atmospheric sulfate species, nonvolatile, and routinely quantified by IC and XRF (through sulfur) within SPARTAN. Potential limitations of this approach are discussed below."

Lines 637-640: "Second, differences in sulfate speciation, including contributions from organosulfur compounds or refractory sulfate salts, may lead to differences between IC-measured water-soluble inorganic sulfate and the AMS sulfate signal."

Lines 643-652: "The second concern is addressed by comparing water-soluble inorganic sulfate measured by IC with total particulate sulfur measured by XRF to identify samples where sulfate speciation may introduce additional uncertainty. Nitrate has also been used as an internal standard in previous offline AMS studies (Srivastava et al., 2021) but presents several challenges for SPARTAN applications, including relatively large potential contributions from organonitrates to

total nitrate (Xu et al., 2015) and more variable and generally lower nitrate concentrations across SPARTAN sites. Therefore, sulfate provides a more robust internal standard for globally distributed SPARTAN samples, and errors associated with using sulfate as the internal standard are expected to be small."

Lines 683-688: "Future applications across SPARTAN will include further evaluation of HOA-dominated environments to assess method performance across a broader range of OA compositions. The method will also be evaluated through comparison with independent OA measurements from complementary techniques, such as FT-IR, providing additional assessment of reconstructed OA across a broader range of atmospheric environments."

Detailed comments:

Line 28: I assume the detection limits refer to a specific filter portion extracted? If yes, please specify this surface. Are the DLs accounting for incomplete solubility?

Reply: The reported detection limits correspond to the extraction of the entire 25 mm Teflon filter (3.53 cm^2 collection area). They are determined from blank filter measurements processed through the same extraction and offline AMS procedure as sample filters. Because these detection limits are based on blank filters rather than ambient aerosol samples or calibration standards with known solubility, they reflect background variability of the analytical method but do not explicitly account for incomplete solubility of ambient aerosol samples. We clarify this in the revised manuscript.

Lines 27-28: "low detection limits (1.7 μg OA and 0.43 μg sulfate per entire filter)"

Lines 171-173: "The entire 25 mm Teflon filter (3.53 cm^2 collection area) is placed aerosol-side up in a 20 mL scintillation vial and covered with 0.2 mL of HPLC-grade methanol followed by 5.8 mL of ultrapure water."

Lines 394-397: "The resulting detection limits are 1.7 μg (0.28 μg/mL extract) for OA and 0.43 μg (0.072 μg/mL extract) for sulfate, expressed as mass per entire filter and reflecting the background variability of the analytical method."

Lines 65-70: How is OC on Teflon filters measured? I thought this is not possible with a Sunset OCEC Analyzer. Are also Quartz filters available? If available the measurements should also be be compared to this OC.

Reply: SPARTAN routinely collects only Teflon filters, and co-located quartz filters are not available. OC on SPARTAN Teflon filters is quantified using Fourier transform infrared spectroscopy (FT-IR) following the standard SPARTAN protocol, rather than using a Sunset OC/EC Analyzer. Briefly, each filter is analyzed in transmission mode over 4000–420 cm^{-1}, and the resulting spectra are converted to absorbance and analyzed using a partial least-squares calibration model developed from paired FT-IR and thermal-optical reflectance (TOR) OC measurements from the Interagency Monitoring of Protected Visual Environments (IMPROVE) network (Debus et al., 2022; Dillner and Takahama, 2015).

FT-IR OC measurements are not available for the offline AMS samples collected in this study, as the co-located online AMS measurements served as the primary reference for method evaluation. For routine SPARTAN filters without co-located online AMS measurements, FT-IR OC provides an independent measurement for comparison with offline AMS results. We add this future comparison with FT-IR measurements as an additional evaluation approach in the revised manuscript.

References:

Debus, B., Weakley, A.T., Takahama, S., George, K.M., Amiri-Farahani, A., Schichtel, B., Copeland, S., Wexler, A.S., and Dillner, A.M.: Quantification of major particulate matter species from a single filter type using infrared spectroscopy – application to a large-scale monitoring network, Atmos. Meas. Tech., 15, 2685–2702, 2022.

Dillner, A.M. and Takahama, S.: Predicting ambient aerosol thermal-optical reflectance measurements from infrared spectra: Elemental carbon, Atmos. Meas. Tech., 8, 4013–4023, 2015.

Lines 685-688: "The method will also be evaluated through comparison with independent OA measurements from complementary techniques, such as FT-IR, providing additional assessment of reconstructed OA across a broader range of atmospheric environments."

Line 114+121: This statement raises the expectation of a substantially superior performance compared to previous studies and needs to be substantiated later in the paper (e.g. Cui et al., https://pubs.acs.org/doi/10.1021/acsestair.4c00051#_i28, Fig. S1). The authors advertise the method as a fast efficient approach. How many samples can in the new approach be measured per day (including time on extractions etc.)?

Reply: We clarify that the goal of this statement is to highlight the advantages of the developed method for application within large-scale monitoring networks such as SPARTAN, rather than to imply improved performance over all previous offline AMS approaches. Accordingly, we revise the manuscript to better compare the performance and applicability of our method with previous offline AMS studies.

SPARTAN filters are processed by cartridge, with each cartridge containing seven PM filter samples and one field blank. Extraction of one cartridge requires approximately 1 hour, while offline AMS analysis requires approximately 2 hours (10 minutes per sample plus 5 minutes of ultrapure water rinsing between samples). Notably, the extraction step has been part of the standard SPARTAN workflow for Ion chromatography (IC) analysis and therefore does not introduce additional sample preparation effort beyond the existing workflow. Under routine operation, 2–3 cartridges can be processed per day, corresponding to approximately 14–21 filter samples daily. We add the sample throughput of the method to the revised manuscript.

Lines 116-117: "However, current offline AMS approaches present practical limitations for routine implementation within large-scale monitoring networks."

Lines 123-126: “These considerations motivate the development of an offline AMS method that is reproducible, operationally streamlined, and compatible with existing SPARTAN protocols for high-throughput routine measurements across globally distributed sites.”

Lines 222-225: “The system is stable and easy to clean and maintain, with carryover removed by nebulizing ultrapure water between samples within a few minutes (Figure S2). Under routine operation, approximately 14–21 filter samples can be analyzed per day, supporting routine analysis of large-scale monitoring networks.”

Line 181: Commonly, samples are directly measured quickly measured after extraction to avoid storage artifacts. Given that the extracts are frozen, a comparison of a selection of samples with and without freezing is needed.

Reply: We thank the referee for raising this point regarding potential storage artifacts. In this study, extracts are frozen prior to offline AMS analysis to facilitate high-throughput measurements and accommodate the processing of large numbers of SPARTAN samples. We carefully store extracts in tightly sealed glass vials, with Teflon tape applied around the interface between the vial and cap, and the vials are further sealed in Ziploc bags. Because all extracts evaluated in this study underwent the same frozen-storage procedure, the online-offline comparison evaluates the performance of the complete workflow as implemented. However, this design does not isolate storage effects or exclude a systematic bias caused by freezing. We agree that a comparison between freshly analyzed and frozen extracts would provide valuable additional information, but this evaluation was not performed in the present study. Future studies will compare freshly analyzed extracts with frozen extracts stored for different durations to further investigate potential storage effects. We explicitly acknowledge the potential influence of storage artifacts as a limitation in the revised manuscript.

Lines 185-188: “The remaining 2 mL aliquot of the filtered extract is transferred to a glass vial, tightly capped, sealed around the cap-vial interface with Teflon tape, placed in a sealed Ziploc bag, and immediately frozen for subsequent AMS analysis to characterize OA, which is the focus of this study.”

Supplement Lines 238-244: “Another potential factor influencing online-offline agreement is extract storage prior to offline AMS analysis. In this study, extracts are frozen prior to measurement to facilitate high-throughput measurements of large numbers of SPARTAN samples. However, the influence of frozen storage has not been independently quantified. Although the comparison with online AMS measurements reflects the overall performance of the workflow, future work will evaluate potential storage artifacts by comparing freshly analyzed extracts with frozen extracts stored for different durations.”

Section 3.1: What is the AMS m/z measurement range?

Reply: The HR-ToF-AMS measurements were acquired over an m/z range of 12–210. We add this information to the revised manuscript accordingly.

Lines 229-232: “In this study, the HR-ToF-AMS is operated in V mode (DeCarlo et al., 2006) over an m/z range of 12–210, providing a mass resolution of approximately 2000–3000 m/Δm and a temporal resolution of 1 minute.”

Line 361: Why is the laboratory blank subtracted before quantifying, i.e. before normalizing to the internal standard on a run-by-run basis?

Reply: The laboratory blank is subtracted from both the OA and sulfate signals before normalization to remove background contributions associated with the extraction and analytical procedures. This ensures that the subsequent organic-to-sulfate normalization is based only on sample-derived signals. In practice, laboratory blanks typically contain only limited amounts of OA and sulfate, so their organic-to-sulfate ratio can be highly variable and dominated by analytical noise. Subtracting OA and sulfate signals before normalization therefore provides a more robust estimate than attempting to normalize the blank itself, which could introduce large uncertainties into OA quantification. We clarify this rationale in the revised manuscript.

Lines 376-378: “Laboratory blank signals for both OA and sulfate are subtracted prior to calculating the organic-to-sulfate ratio to remove analytical background contributions before normalization.”

line 384: it would be best to also report detection limits in ug/ml extract.

Reply: We add the corresponding detection limits in units of µg/mL extract to the revised manuscript.

Lines 394-397: “The resulting detection limits are 1.7 µg (0.28 µg/mL extract) for OA and 0.43 µg (0.072 µg/mL extract) for sulfate, expressed as mass per entire filter and reflecting the background variability of the analytical method.”

Line 392: Was this exercise performed based on teflon filters collected in the same way as for SPARTAN?

Reply: Yes. The offline samples in this study were collected using the same sampling configuration as the standard SPARTAN protocol, including the same sampling stations, cartridge configuration, and filter handling procedures. The only differences were the sampling flow rate, which changes the particle size cut as discussed in the response to the next comment, and the sampling duration, which changes the collected aerosol mass. These parameters were adjusted to facilitate comparison with co-located online AMS measurements. Therefore, the results are most directly representative of routine SPARTAN measurements. We clarify this in the revised manuscript.

Lines 410-412: “Filter sampling was performed using SPARTAN stations following the standard SPARTAN protocol, with the stations operating continuously and sampling for 24 hours per filter at flow rates ranging from 6 to 11 L/min.”

Line 400: Given that the AMS was equipped with a PM1 lense, was PM1 sampled on the filters in the end? As this point is a bit unclear to me, a clarification would be helpful.

Reply: We intentionally collected offline filter samples with PM_1, $PM_{2.5}$, and intermediate size cuts by varying the sampling flow rate through the cyclone. The standard SPARTAN protocol collects $PM_{2.5}$ samples, whereas the online AMS measures non-refractory PM_1. Therefore, PM_1 filter samples were collected to provide a more direct comparison with online AMS measurements, $PM_{2.5}$ filter samples were collected to represent routine SPARTAN sampling conditions, and intermediate size cuts were additionally included to assess the influence of particle size cut on offline AMS measurements. We find that particle size cut has only a minor influence on the online-offline agreement, as filters collected between PM_1 and $PM_{2.5}$ size cuts exhibit comparable OA recoveries (Figure S17). We clarify this in the revised manuscript.

Lines 412-414: “The collected filters included PM_1, $PM_{2.5}$, and intermediate size cuts, corresponding to the PM_1 cyclone cutoff at 11 L/min and the $PM_{2.5}$ cyclone cutoff at 5 L/min.”

Fig 4: Given that OA is quite oxygenated, an overall good agreement can be expected for the extracts. With the global scope of the method, how well does the method perform for locations with substantially higher contributions of hydrocarbons?

Reply: We appreciate this insightful question. The current study does not directly evaluate method performance at sites dominated by HOA, and assessment under such conditions will require future studies in environments with substantially higher HOA contributions.

To account for variations in OA composition and water solubility across globally distributed sites, we do not rely only on directly measured offline OA. Instead, we reconstruct ambient OA using offline-derived OOA and HOA together with their corresponding factor recoveries. As a result, the agreement between reconstructed OA and online OA (Figure 7, slope = 0.98 and r^2 = 0.67) is substantially improved compared with the direct comparison between offline OA and online OA (Figure 3, slope = 0.44 and r^2 = 0.57), indicating that this reconstruction approach can help account for the composition-dependent differences in OA recovery. Compared with OOA-dominated samples, HOA-rich samples are expected to have lower measured offline OA concentrations due to the lower water solubility of hydrocarbon-like species. The reconstruction approach compensates for this lower OA recovery by applying factor-specific recovery corrections. For samples examined in this study, the HOA fraction determined from online AMS measurements covers a relatively wide range (10–56 %), and reconstructed OA shows generally good agreement with online OA across this range, supporting the applicability of this approach across varying OA compositions. However, we acknowledge that reconstructed OA is expected to have greater uncertainty at sites dominated by HOA, as HOA recovery is more variable than OOA recovery.

Future applications of this offline method across SPARTAN will pay particular attention to HOA-dominated sites to further evaluate method performance across diverse OA compositions. We explicitly acknowledge this limitation in the revised manuscript.

Lines 681-688: "However, greater uncertainty is expected at sites with high HOA contributions because HOA exhibits more variable recovery. Future applications across SPARTAN will include further evaluation of HOA-dominated environments to assess method performance across a broader range of OA compositions. The method will also be evaluated through comparison with independent OA measurements from complementary techniques, such as FT-IR, providing additional assessment of reconstructed OA across a broader range of atmospheric environments."

Line 480: Some further validation and discussion of the PMF solutions is needed in the SI to evaluate it (e.g. comparison of HOA vs BClf or NOx and OOA vs secondary inorganic aerosols).

Reply: We thank the referee for this suggestion. We have substantially expanded the PMF discussion in the revised Supplement (Text S3 and S4) by providing a more comprehensive evaluation of PMF diagnostics, including factor-number selection, rotational ambiguity, residuals, and comparisons with higher-order solutions (Figure S7). We further validate the selected factors through temporal comparisons with characteristic tracer ions and secondary inorganic species (Figure S8). Detailed responses and the corresponding manuscript revisions are included in our reply to Major Comment 1 and are not repeated here.

Line 482: In addition, this study and the cited ones assume that OA factors have the same AMS mass spectrum in online and offline measurements. This should be stated as an assumption explicitly.

Reply: Following the revisions made in response to Major Comment 1, we now evaluate several approaches for deriving offline OOA and HOA, each involving different assumptions regarding the similarity of online and offline factor profiles. Specifically, we include (1) HOA-only constrained PMF, in which the HOA profile is constrained to the corresponding online factor profile with *a*-values of 0, 0.1, 0.3, and 0.5 while the OOA profile is allowed to vary freely; (2) constrained PMF with both OOA and HOA constrained to the corresponding online factor profiles using the same range of *a*-values; and (3) weighted NNLS regression, which assumes fixed OOA and HOA factor profiles. Thus, identical online and offline factor profiles are assumed only for the fully constrained cases (*a*-value = 0) and the weighted NNLS regression, whereas increasing *a*-values in the constrained PMF analyses relax this assumption by allowing the factor profiles to deviate from the online references. We have explicitly stated these assumptions in the revised manuscript and Supplement where applicable. Additional details are provided in our response to Major Comment 1 and are not repeated here.