Response to reviewer comments

We thank the three reviewers very much for their helpful comments and suggestions. Addressing these comments has substantially improved the quality of the manuscript. We have provided responses and necessary revisions to each reviewer comment below.

Reviewer #1

Missing data in $PM_{2.5}$ speciation monitoring, due to instrumental drift, calibration, and maintenance, poses challenges for source apportionment and health risk assessments. Conventional imputation methods, including statistical techniques and deep learning, depend on mathematical correlations and often lack physical interpretability. This study presents a novel Positive Matrix Factorization-based reconstruction method (PMFr) that integrates source profile characteristics into the imputation process. Unlike traditional models that rely solely on data covariance, this approach uses "low-entropy structures" to reconstruct latent information, ensuring chemical consistency and physical interpretability. Given its potential to improve data quality in atmospheric research, the reviewer recommends this work for publication with some revisions and clarifications.

Major Comments:

Comment #1:

The manuscript introduces a novel framework for data imputation based on low-entropy structures, but lacks practical guidelines on its limits of applicability for specific timestamps. It does not define conditions under which the method may fail due to insufficient observational constraints. The methodology assumes the source contribution vector (G) can be uniquely resolved from observed species, which requires at least one key tracer species for each source factor. However, the manuscript does not address scenarios where all characteristic species for a specific source are missing, leading to an under-constrained system that undermines the imputation's reliability.

The authors should include a section on practical principles for validity checks. It must state that before imputation, users should ensure each identified source factor has at least one non-missing key tracer. If any time point lacks all diagnostic tracers for a source, that data point should be flagged as un-imputable or handled with caution.

To operationalize this principle, the authors should add a table listing the "Non-Missable Key Tracers" for each “pollution source”. This table should clearly map each source factor to its essential diagnostic species. This will serve as a vital reference for practitioners to assess data quality and imputation feasibility before applying the model.

Addressing these points is essential to prevent the misapplication of the method and to clarify the boundary conditions under which the proposed imputation remains scientifically valid.

Response:

We sincerely thank the reviewer for this important comment. We agree that the availability of key tracers is critical for PMFr, because the source contribution vector (G) needs to be sufficiently constrained by source-specific chemical information. When all diagnostic tracers for a specific source factor are simultaneously missing at a given timestamp, the corresponding G vector becomes less constrained by observations, and the reliability of the reconstruction should be carefully evaluated.

We would like to clarify that this situation is one of the motivations for including the pre-imputation step in PMFr. When all tracers associated with a specific factor are missing, PMFr first uses a pre-imputation method to provide an initial estimate for the missing tracer values, allowing the subsequent PMF run to proceed. In this study, KNN is recommended for this initial step because of its simplicity, efficiency, and ability to provide a reasonable initial estimate of temporal variation. The subsequent PMFr reconstruction then further constrains the imputed values using PMF-resolved source profiles and source-receptor relationships. Therefore, such cases are not automatically treated as unusable; rather, they are considered cases with weakened source constraints and should be flagged and handled with caution. Our sensitivity analysis (Text S5 and Table S14) further shows that PMFr can still outperform baseline methods when the pre-imputation step provides a reasonable estimate of the general temporal variation of the missing species.

To address the reviewer's concern and to prevent misapplication of the method, we have revised the manuscript as detailed below:

1. **Listing Non-Missable Key Tracers (Table S13):** We have added **Table S13** in the Supplementary Information, which maps each PMF-resolved pollution source in this study to its essential diagnostic species. This table provides a practical reference for users to evaluate whether each source factor retains sufficient observational constraints before applying PMFr. When PMFr is applied to other datasets or to other species requiring imputation, the non-missable key tracers should be checked based on the resolved source profiles and prior knowledge of local source characteristics.

Table S13. Pollution sources and corresponding non-missable key tracers

Factor Identity	Non-Missable Key Tracers
Secondary Nitrate	NH_4^+, NO_3^-
Secondary Sulfate	NH_4^+, SO_4^{2-}
On-road Traffic	OC, EC, Ba, Cu
Coal Combustion	OC, EC, As, Se, K, Pb
Metal Smelting	Mn, Pb, Cr, Ni, Zn
Heavy Oil Combustion	V, Ni
Crustal Dust	K, Fe, Ca, Si, Ti

2. **Adding a validity-check procedure in Section 2.3 (Line 106-111):** We have revised the Methods section to explicitly state that, before PMFr reconstruction, the availability of key tracers or co-tracers should be checked at each timestamp to identify cases with weakened source constraints. This check helps users determine whether the source contribution vector (G) is sufficiently constrained by observed species or whether initial estimation (e.g., KNN) is required for the PMF reconstruction.

"When imputing tracers, the availability of co-tracers should be checked at each timestamp before reconstruction, because the source contribution vector (G) needs to be constrained by source-specific tracer information. If all tracers associated with a specific factor are simultaneously missing, the corresponding G vector is less directly constrained by observed species; in such cases, these missing tracer values are first imputed using another imputation method, with KNN recommended for its simplicity, efficiency, and ability to provide a reasonable estimate of temporal variation. The corresponding uncertainty is set to 10% of the imputed concentration. For missing tracers with available co-tracers, as well as for non-tracers, missing values are replaced by the geometric mean."

3. **Expanding the discussion of applicability and limitations in Section 3.4 (Line 292-306):** We have added a dedicated discussion in the revised Section 3.4, "Applicability and Limitations of PMFr", to clarify the significance of validity checks. In this section, we state that PMFr is most reliable when at least one key tracer remains available for each source factor. If all key tracers for a specific source are simultaneously missing, the corresponding G vector is less directly constrained by observed species and the resulting reconstruction should be

interpreted with caution. We also clarify that the pre-imputation step is designed to provide the initial estimate needed for PMFr reconstruction under such weakened source-constraint conditions.

"PMFr is applicable when source-related chemical structures can be constrained by at least one tracer for each source factor, and the completed dataset is suitable for subsequent source apportionment analysis.

One limitation of PMFr is related to missing patterns in which source-related constraints become insufficient. As shown in Table S7, the performance of PMFr declines when the missing pattern shifts from MCMI to MCMS. For NH_4^+ at a 10% missing rate, the MAPE increases from 9.57% under MCMI to 20.67% under MCMS, and the IoA decreases from 0.98 to 0.95. For NO_3^- at a 10% missing rate, the MAPE increases from 14.82% under MCMI to 23.92% under MCMS. At a 20% missing rate, the MAPE increases from 13.63% to 25.87% for NH_4^+, and from 22.81% to 28.46% for NO_3^-. As shown in Table S6, when OC and EC are simultaneously missing, the performance of PMFr becomes comparable to that of baseline methods. For instance, at a 10% missing rate, the R^2 values for OC are 0.73 for PMFr, 0.74 for DBN, 0.68 for KNN, and 0.66 for BPCA. For EC, R^2 values are 0.84 for PMFr, 0.85 for BPCA, 0.80 for DBN, and 0.79 for KNN. Fundamentally, PMFr assumes that the source contribution vector (G) can be sufficiently constrained by observed species, which requires at least one key tracer for each factor. The key tracers used for imputation and source identification are shown in Table S13. If all key tracers for a specific source are simultaneously missing, the corresponding source contribution vector G is less directly constrained by observed species and should be interpreted with caution. Nevertheless, sensitivity analysis indicates that PMFr can still outperform baseline methods when the pre-imputation step provides a reasonable estimate of the general temporal variation of the missing species (Text S5 and Table S14)."

Comments #2:

Mixed missing data patterns (MCMS vs. MCMI) in Cases 4~8. MCMS is inherently much more challenging than MCMI because it removes the identifiability of the source, whereas MCMI only removes temporal continuity. A model might perform well under MCMI but fail catastrophically under MCMS. Combining these two patterns into a single performance metric for each Case obscures the specific source of error. Therefore, the reviewer suggests that reporting the results for pure MCMS scenarios and pure MCMI scenarios separately is more scientifically valid.

Response:

We appreciate the reviewer's rigorous comment. The reviewer is correct from a theoretical standpoint: MCMS and MCMI represent fundamentally different mechanisms of information loss, and isolating them is highly valuable for understanding specific algorithmic vulnerabilities.

Regarding the main text, our primary goal in proposing the PMFr framework is to provide a robust, practical imputation tool tailored for realistic, operational datasets. In actual continuous monitoring stations, complex instrument malfunctions frequently result in a simultaneous occurrence of both MCMS and MCMI. Therefore, Cases 4-8 in the main manuscript were designed to evaluate whether PMFr can maintain its reconstruction stability when both mechanisms occur simultaneously, which is precisely the challenge faced in practice.

However, we fully agree with the reviewer that reporting the isolated scenarios provides essential scientific insights. To address this concern without diluting the real-world focus of the main manuscript, we have now provided the evaluations in the **Section 3.4 Applicability and Limitations of PMFr**—the **most challenging** MCMS scenario, in which all key tracers are missing simultaneously, and the corresponding MCMI scenario. Specifically, the detailed performance metrics for all original mixed cases are already comprehensively listed in **Supplementary Tables S7-S12**.

The added discussion comparing MCMS and MCMI reads as follows (Line 293-306):

"One limitation of PMFr is related to missing patterns in which source-related constraints become insufficient. As shown in Table S7, the performance of PMFr declines when the missing pattern shifts from MCMI to MCMS. For NH_4^+ at a 10% missing rate, the MAPE increases from 9.57% under MCMI to 20.67% under MCMS, and the IoA decreases from 0.98 to 0.95. For NO_3^- at a 10% missing rate, the MAPE increases from 14.82% under MCMI to 23.92% under MCMS. At a 20% missing rate, the MAPE increases from 13.63% to 25.87% for NH_4^+, and from 22.81% to 28.46% for NO_3^-. As shown in Table S6, when OC and EC are simultaneously missing, the performance of PMFr becomes comparable to that of baseline methods. For instance, at a 10% missing rate, the R^2 values for OC are 0.73 for PMFr, 0.74 for DBN, 0.68 for KNN, and 0.66 for BPCA. For EC, R^2 values are 0.84 for PMFr, 0.85 for BPCA, 0.80 for DBN, and 0.79 for KNN. Fundamentally, PMFr assumes that the source contribution vector (*G*) can be sufficiently constrained by observed species, which requires at least one key tracer for each factor. The key tracers used for imputation and source identification are shown in Table S13. If all key tracers for a specific source are simultaneously missing, the corresponding source contribution vector *G* is less directly constrained by observed species and should be interpreted with caution. Nevertheless, sensitivity analysis indicates that PMFr can still outperform baseline methods when the pre-imputation step provides a reasonable estimate of the general temporal variation of the missing species (Text S5 and Table S14)."

Comments #3:

The PMFr method relies on the assumption that source chemical profiles remain stable over time. However, real-world atmospheric conditions lead to dynamic source signatures that can vary significantly due to seasonal changes, fuel composition, and combustion conditions. This variability can introduce biases in reconstructed data if profiles differ from reality. Though this study uses a short two-month dataset, concerns about using this method over longer periods (e.g., multi-year datasets) highlight issues with profile stability. The manuscript currently lacks guidance on determining the appropriate temporal window for stable profiles. The reviewer advises the authors to provide clear, quantitative guidelines for assessing this assumption, including metrics or statistical tests (like rolling window analysis or change-point detection) to identify when profiles need recalibration or updating.

Response:

We thank the reviewer for this thoughtful comment. Indeed, PMFr does rely on the assumption that source chemical profiles remain sufficiently stable within the reconstruction period. If source profiles change substantially over time, the source-receptor relationships resolved by PMF may no longer represent the true receptor-based pollution sources, which could introduce biases into the reconstructed data. This is a key limitation of PMFr.

In the present study, we intentionally used a relatively short two-month dataset to reduce the potential influence of long-term source-profile changes. Within such a short period, source profiles are more likely to remain stable, making the PMF-resolved source-receptor relationships suitable for missing-value reconstruction. As mentioned by the reviewer, source-profile changes may occur under various real-world conditions, such as changes in fuel composition, implementation or removal of end-of-pipe control technologies, changes in industrial production processes, shutdown or relocation of major emission sources, changes in source suppliers, or strong seasonal shifts in atmospheric processing. Therefore, the appropriate temporal window for applying PMFr should not be fixed universally, but should be determined according to the stability of source profiles in the specific dataset and the local emission context.

To address this concern, we have revised the manuscript by adding a dedicated discussion in the Section 3.4 "**Applicability and Limitations of PMFr**" section (Line 319-328). In this section, we now explicitly state that source-profile stability should be evaluated before applying PMFr to extended datasets. We further discuss that rolling PMF approaches can be used to examine temporal changes in source profiles and to determine whether the PMF solution remains stable over time. Because real-world source-profile changes are often not known a priori, we believe that such diagnostic checks are essential for long-term applications. When substantial changes in source profiles are detected, the dataset should be divided into shorter time windows, or the PMF model should be recalibrated before applying PMFr. Future improvements of PMFr could also incorporate time-dependent source profiles to better support reconstruction under changing atmospheric conditions.

The corresponding revision has been added to Section 3.4, "Applicability and Limitations of PMFr", as follows (Line 319-328):

"Another limitation of the PMFr framework lies in the assumption of relatively stable source profiles. In PMFr, source profiles are assumed to remain stable so that the source-receptor relationships resolved by PMF can be used to guide missing-value reconstruction. This assumption is generally more reasonable for short-term datasets, but it may become weaker for long-term datasets, especially those spanning multiple years, during which emission patterns may change substantially. Therefore, source-profile stability can be evaluated before applying PMFr in extended applications. As for long-term data applications, moving-window evolving PMF approaches provide a promising way to track time-dependent factor profiles within short moving windows. Improvements of PMFr could incorporate time-dependent source profiles to address this limitation and better support reconstruction under changing source emissions."

Comments #4:

The PMFr framework relies on a linear mixing model (C=G×F), assuming observed concentrations are linear combinations of primary emissions. However, secondary components like sulfates, nitrates, and Secondary Organic Carbon (SOC) arise from complex, non-linear photochemical reactions, which the linear assumption may fail to accurately capture, particularly during heavy pollution or specific weather conditions. The manuscript does not sufficiently address the uncertainty introduced by this assumption in reconstructing secondary species. It is recommended that the authors discuss the limitations of the linear model in secondary aerosol formation and consider conducting a sensitivity analysis to quantify the uncertainty.

Response:

We thank the reviewer for raising this important point. The linear mixing model used in PMFr cannot explicitly quantify or simulate the nonlinear photochemical reactions responsible for the formation of secondary components. However, PMFr is not intended to model the chemical reaction pathways of secondary aerosol formation. Instead, similar to conventional PMF receptor modeling, PMFr uses the observed chemical dataset to quantify the amount of secondary particles whose temporal variations differ from those of primary sources. These different temporal patterns allow secondary components to be identified as separate PMF factors. Therefore, PMFr uses the PMF-resolved secondary particles to quantify the abundance of already formed secondary components rather than simulating their nonlinear formation pathways. In this way, PMFr can be used for imputing missing secondary species without explicitly parameterizing the complex and nonlinear reactions that produced them.

Minor Comments:

Comments #1:

Line 82. MCMS and MCMI should be defined in the first paragraph of section 2.2.

Response:

Revised as suggested.

Comments #2:

Figure 1b illustrates model performance metrics through a scatter plot comparing MAPE (y-axis) and IoA (x-axis), with R^2 values annotated. However, it does not visualize the standard deviation (σ) of modeled data against observations. A model may show high IOA and low MAPE but still misrepresent variability, indicating "amplitude bias," which is crucial for accurate source contribution estimates. The authors should include a Taylor Diagram as a supplementary figure for a comprehensive statistical assessment of variance and correlation in the observed data.

Response:

We have generated a Taylor diagram (**Figure S31**) as a supplementary figure to visualize the variance and correlation. The diagram indicates that the PMFr reconstructed data yield a normalized standard deviation of 0.93, compared to the observational reference (σ = 1.0).

To systematically present this comprehensive statistical assessment, we have optimized the manuscript structure by introducing a new section, "Section 3.2.1 Overall Performance under All Missing Scenarios". The quantitative evaluation of the Taylor diagram and the corresponding variance assessment have been fully integrated into this new section.

The revised text in Section 3.2.1 is as follows (Line 170-178):

"As shown in Figure S30, the PMFr method achieves the overall R^2 of 0.81 and MAPE of 22.8% under the three evaluated missing scenarios. In comparison, DBN results in an R^2 of 0.73 and a MAPE of 32.2%, BPCA yields an R^2 of 0.72 and a MAPE of 30.6%, and KNN achieves an R^2 of 0.72 and a MAPE of 31.2%. For simple baseline methods, LI produces an R^2 of 0.35 and a high MAPE of 61.7%, while the Mean imputation method results in a higher MAPE of 66.75%. Given that mean imputation produces a constant value without temporal variation and consistently fails to provide effective reconstruction across individual scenarios (Figures S11-S29), its performance is solely quantified by MAPE here and is excluded from further detailed comparisons in subsequent sections. Furthermore, the Taylor diagram (Figure S31) illustrates that the PMFr reconstructed data yield a normalized standard deviation (σ) of 0.93, closely matching the observational variance (σ = 1.0), suggesting its capability to capture the amplitude of data variations.”

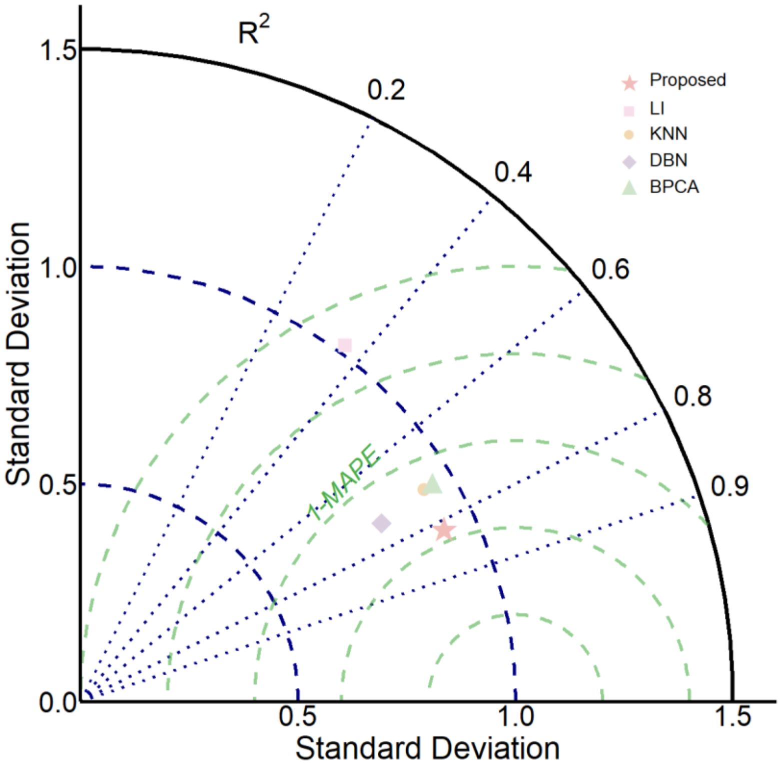


Figure S31. Taylor diagram summarizing the statistical performance of the proposed and baseline imputation models.

Reviewer #2

This manuscript proposes a PMF-based reconstruction method (PMFr) for imputing missing values in $PM_{2.5}$ speciation datasets by explicitly using source-receptor relationships, rather than relying solely on conventional statistical or machine-learning approaches. The study is interesting and potentially valuable, particularly because it does not evaluate imputation quality only in terms of reconstruction error, but also examines whether the reconstructed dataset preserves consistency in subsequent source apportionment results. This is a meaningful strength of the work. The comparison with several benchmark methods under multiple missing-data scenarios is also generally appropriate.

However, the manuscript still requires revision before it can be considered for publication. The paper shows clear promise, but some of the claims are broader than what is fully supported by the presented analysis, and several parts of the interpretation would benefit from more careful and balanced framing. In particular, the manuscript should more clearly distinguish the conditions under which PMFr performs especially well from those under which its advantage is limited, and it should present the generalizability of the method more cautiously in light of the assumptions underlying PMF-based reconstruction.

Major Comments:

Comment #1:

The method is evaluated using data from a single urban site over a limited observational period and for a specific set of $PM_{2.5}$ chemical species. However, the conclusion extends the potential applicability of PMFr to other atmospheric datasets, including VOC-related contexts. While this extension may be reasonable as a future possibility, the current manuscript does not yet demonstrate such breadth. I suggest that the authors moderate the scope of their claims and more clearly state that the present findings support the method under the conditions tested in this study.

Response:

We agree that our original conclusion overstated the breadth of the PMFr method by extending its applicability to other datasets (e.g., VOCs) without empirical demonstration in the current study. To address this, we have carefully revised the Conclusion section to strictly constrain the scope of our claims.

Our revised Conclusions section is detailed below (Line 330-341):

"We developed a physically interpretable imputation method (PMFr) for reconstructing missing $PM_{2.5}$ speciation data by leveraging source-receptor relationships encoded in key chemical species. Benchmarking against commonly used imputation techniques, including Mean, LI, KNN, BPCA, and a deep learning predictive model, demonstrates that PMFr achieves improved accuracy and robustness while preserving physical and chemical interpretability, especially for key marker species. Crucially, the PMFr-completed dataset is better suited for subsequent PMF source apportionment because it preserves source-profile composition and source-contribution temporal features. Nevertheless, the advantage of PMFr may become less substantial when source-related constraints are weakened, such as when all key tracers for a specific source factor are simultaneously missing, or when baseline methods can already capture stable co-variation patterns for certain species. These chemically consistent and physically meaningful estimates also rely on the temporal stability of source chemical compositions. Recognizing the limitations of such static assumptions for long-term datasets, we highlight the necessity of systematically verifying source stability in extended applications. Therefore, this work offers a simple and generalizable solution that strengthens the reliability of real-world speciation datasets and enhances their suitability for source apportionment and policy-relevant analyses."

Comment #2:

Several explanations offered for species-specific performance differences are plausible and scientifically sensible, but they are still interpretive rather than directly demonstrated. For example, the discussion of lower sulfate performance, or the explanation of differential behavior for OC/EC and NH_4^+/NO_3^-, seems to go beyond the evidence shown in the main performance metrics. These interpretations should be framed more cautiously, using language such as "may reflect," "is likely associated with," or "is consistent with," unless additional analysis is provided to directly support those mechanistic explanations.

Response:

Following the reviewer's suggestion, we have carefully reviewed the discussion section and moderated the scope of our claims. We have replaced definitive causal language with more cautious and nuanced phrasing to accurately reflect that these explanations are plausible hypotheses rather than directly proven mechanisms.

The corresponding modifications in the revised manuscript are detailed below:

1. Original text: The absence of other cations like Na^+ and Mg^{2+} impact the imputation efficiency when missing SO_4^{2-} concentration values are high. The formation of NH_4NO_3 dominates nitrate, while $(NH_4)_2SO_4$ account for only part of sulfate.

   Revised Text (Line 188-190): The absence of other cations like Na^+ and Mg^{2+} may impact the imputation efficiency when the missing SO_4^{2-} concentrations are high. This difference is likely because the formation of NH_4NO_3 typically dominates nitrate, while $(NH_4)_2SO_4$ accounts for only a portion of the total sulfate.
2. Original Text: EC is primarily emitted from motor vehicles, whereas OC consists of both primary organic carbon (POC) and secondary organic carbon (SOC); POC

is directly emitted, while SOC forms in the atmosphere through secondary processes. POC can partially originate from motor vehicles, whereas SOC is associated with secondary sources such as SS and SN

Revised Text (Line 203-206): EC is primarily emitted from motor vehicles, whereas OC encompasses both directly emitted primary organic carbon (POC) and secondary organic carbon (SOC) formed through atmospheric processes. The behavior of POC is consistent with partial origins from vehicular emissions, while the variations of SOC are likely associated with secondary sources such as SS and SN.

3. Original Text: The decline is attributable to the absence of key tracers, consistent with the tracer-dependent variability observed at the NEPB site—where the strong OC-EC correlation reflects their common origin in motor-vehicle emissions. PMFr is affected because PMF overestimate the loading of OC and EC in the OT factor, thereby underscoring their contributions from other sources.

   Revised Text (Line 220-223): The decline is likely attributable to the absence of key tracers, consistent with the tracer-dependent variability observed at the NEPB site—where the strong OC-EC correlation may reflect their common origin in motor-vehicle emissions. The performance of PMFr may be impacted because PMF tends to overestimate the loading of OC and EC in the OT factor, thereby obscuring their contributions from other sources.

4. Original Text: This improvement arises because Ti is predominantly emitted from dust sources, enabling PMFr to estimate missing values using the characteristic Ti-Ca-Si ratios in source profiles once the CD factor is identified

   Revised Text (Line 233-235): This improvement is likely associated with the predominant emission of Ti from dust sources, enabling PMFr to estimate missing values by leveraging the characteristic Ti-Ca-Si ratios in source profiles once the CD factor is identified.

5. The performance of DBN declines for ionic species due to insufficient valid training samples and variables caused by long missing gaps and increasing number of missing specie (Figures S22, S23, S24, and S25). NH_4^+ and NO_3^- are strongly correlated due to the predominance of NH_4NO_3 during fall in NEPB site.

   Revised Text (Line 247-249): The performance of DBN declines for ionic species, which may be attributed to insufficient valid training samples and variables caused by long missing gaps and an increasing number of missing species (Figures S22–S25). Furthermore, NH_4^+ and NO_3^- are strongly correlated, a pattern consistent with the predominance of NH_4NO_3 during the fall at the NEPB site.

Comment #3:

One of the strengths of the manuscript is that it does not hide the fact that PMFr is not uniformly superior in every situation. There are cases in which performance is weaker, or where the gap between PMFr and alternative methods narrows. These include certain species such as sulfate, situations involving high Fe concentrations, and some scenarios involving medium gaps or instrument-failure-type missingness. These limitations are scientifically important and should be more explicitly synthesized in the discussion. A dedicated paragraph or subsection on the strengths and limitations of PMFr across species types and missingness patterns would make the manuscript more informative and more credible.

Response:

To address this comment, we have added a dedicated subsection, Section 3.4 "Applicability and Limitations of PMFr", to synthesize the strengths and limitations of PMFr across species types and missingness patterns. In this section, we clarify that PMFr is most applicable when source-related chemical structures can be constrained by at least one tracer for each source factor, and when the imputed dataset is intended for subsequent source apportionment analysis.

We further discuss the situations in which the advantage of PMFr becomes less substantial. First, when the missing pattern shifts from MCMI to MCMS, source-related observational constraints become less robust because multiple species are absent at the same timestamp. Under this condition, the corresponding source contribution vector (G) is less directly constrained by observed species, and the reconstruction should be interpreted with caution. We therefore added quantitative examples showing that the performance of PMFr declines from MCMI to MCMS for NH_4^+ and NO_3^-, while also noting that sensitivity analysis indicates that PMFr can still outperform baseline methods when the pre-imputation step provides a reasonable estimate of the general temporal variation of the missing species.

Second, we discuss species for which the advantage of PMFr is less substantial, including SO_4^{2-} and crustal elements such as Ca, Si, and Fe. For crustal elements, baseline methods can become competitive because these species are primarily emitted directly and often exhibit relatively stable inter-variable correlations.

Importantly, we also emphasize that comparable concentration-level performance does not necessarily imply that baseline methods are equally reliable for further source apportionment. To demonstrate this point, we added a downstream PMF evaluation section, **"3.3 Assessing the Impact of Imputation on PMF Source Apportionment".** In this section, we selected two representative cases where the advantage of PMFr became less pronounced: SO_4^{2-} missingness in Case 2 and high-concentration Fe missingness in Case 5. By comparing PMF-resolved source profiles and source contributions derived from different imputed datasets with those from the complete dataset, we showed that PMFr better preserved source-profile composition and source-contribution temporal patterns. These results clarify that the value of PMFr lies not only in direct concentration reconstruction, but also in preserving source-related chemical and temporal structures required for physically interpretable PMF analysis.

The following text has been added to Section 3.4 of the revised manuscript:

"Applicability and Limitations of PMFr (Line 292-318):

PMFr is applicable when source-related chemical structures can be constrained by at least one tracer for each source factor, and the completed dataset is suitable for subsequent source apportionment analysis. One limitation of PMFr is related to missing patterns in which source-related constraints become insufficient. As shown in Table S7, the performance of PMFr declines when the missing pattern shifts from MCMI to MCMS. For NH_4^+ at a 10% missing rate, the MAPE increases from 9.57% under MCMI to 20.67% under MCMS, and the IoA decreases from 0.98 to 0.95. For NO_3^- at a 10% missing rate, the MAPE increases from 14.82% under MCMI to 23.92% under MCMS. At a 20% missing rate, the MAPE increases from 13.63% to 25.87% for NH_4^+, and from 22.81% to 28.46% for NO_3^-. As shown in Table S6, when OC and EC are simultaneously missing, the performance of PMFr becomes comparable to that of baseline methods. For instance, at a 10% missing rate, the R^2 values for OC are 0.73 for PMFr, 0.74 for DBN, 0.68 for KNN, and 0.66 for BPCA. For EC, R^2 values are 0.84 for PMFr, 0.85 for BPCA, 0.80 for DBN, and 0.79 for KNN. Fundamentally, PMFr assumes that the source contribution vector (G) can be sufficiently constrained by observed species, which requires at least one key tracer for each factor. The key tracers used for imputation and source identification are shown in Table S13. If all key tracers for a specific source are simultaneously missing, the corresponding source contribution vector G is less directly constrained by observed species and should be interpreted with caution. Nevertheless, sensitivity analysis indicates that PMFr can still outperform baseline methods when the pre-imputation step provides a reasonable estimate of the general temporal variation of the missing species (Text S5 and Table S14). The numerical advantage of PMFr is less substantial for certain species such as SO_4^{2-} and crustal elements. For crustal elements, baseline methods can become competitive because these species are primarily emitted directly and usually exhibit relatively stable inter-variable correlations. As shown in Table S5, when imputing Ca, Si, and Fe at a 15% missing rate, several statistical or machine-learning methods perform comparably to PMFr. For Ca, the R^2 values are 0.93 for PMFr, 0.91 for BPCA, and 0.90 for DBN. For Si, PMFr achieves an R^2 of 0.82, which is matched by DBN and closely followed by KNN (0.79). For Fe, the R^2 values are 0.83 for PMFr, 0.86 for DBN, 0.84 for KNN, and 0.84 for BPCA, with DBN and KNN achieving slightly higher IoA values than

PMFr. This reduced separation suggests that statistical or machine-learning methods can capture stable co-variation patterns among some primary species, thereby reducing the relative advantage of the source-constrained PMFr method for these specific cases. However, comparable concentration-level performance does not necessarily imply that baseline methods are equally reliable for source apportionment. The PMF evaluation results showed that PMFr better preserved source-profile composition and source-contribution temporal patterns, even in representative cases where direct imputation metrics became comparable among methods."

Comment #4:
The manuscript provides multiple reasons for adopting the 7-factor solution, including interpretability, residual behavior, and diagnostic stability. However, the current presentation reads more as a list of supporting points than as a clearly structured argument. The authors should revise this section so that the decision logic becomes easier to follow. For example, the discussion could more explicitly distinguish why the lower-factor solutions were insufficient, why the higher-factor solutions were over-resolved or physically less meaningful, and why the selected solution best balanced interpretability and statistical diagnostics.

Response:
We sincerely thank the reviewer for this constructive suggestion. In the revised manuscript, we have reorganized Section 3.1 to explicitly follow a decision logic that contrasts the 7-factor solution with alternative scenarios. Specifically:

1. **4-6 factor solutions:** We now explicitly state that these were statistically insufficient, as evidenced by a sharp decline in the Q/Q_{exp} ratio (11.2%) when increasing to 7 factors, and physically inadequate due to the improper lumping of distinct sources like traffic and secondary sulfate.
2. **8-9 factor solutions:** We clarify that these led to statistical over-resolution with diminishing returns in Q/Q_{exp} improvements and significant instability (high BS unmapped rates). Physically, these solutions resulted in uninterpretable splitting of stable sources like coal combustion.
3. **Optimal 7-factor solution:** We demonstrate how this solution best balances robust statistical diagnostics with clear, physically meaningful source identification.

The revised text is provided below (Line 130-166):
"PMF solutions were explored with four to nine factors using datasets containing 10% missing values. The best-fitting solution was selected by the model performance,

including the interpretability of the factor profiles, which is the key basis for determining the optimal factor number and imputation, and the distributions of scaled residuals (Figures S2 and S3). Bootstrapping (BS), displacement (DISP), and combined BS-DISP analyses were also performed for these solutions. Four-to-six factor solutions were statistically insufficient to fully explain the variance in the input data matrix. When the factor number increased from six to seven, the Q/Q_{exp} ratio experienced a decline of 11.2%. This drop indicates that the 6-factor model leaves a substantial amount of residual variance unexplained. Because of this lack of statistical resolution, these lower-factor solutions failed to effectively decouple distinct emission sources. Specifically, the 5-factor solution improperly lumped on-road traffic (OT) emissions with metal smelting (Figure S5). In the 6-factor solution, sulfate and nitrate were mixed together as a single identified secondary inorganic aerosol factor (Figure S6). Eight and nine factor solutions demonstrated statistical over-resolution with diminishing returns. As the factor number increased from seven to eight, the Q/Q_{exp} ratio dropped less dramatically (8.5%) compared to the previous step. Furthermore, the 8-factor solution exhibited a high unmapped rate during the BS analysis, highlighting severe statistical instability. From a physical perspective, these higher-factor solutions over-resolved the data into physically meaningless components. For instance, the 8-factor solution isolated a Cu-high loading factor that lacks a clear chemical profile (Figure S7), while the 9-factor solution further fragmented the coal combustion source into two unidentifiable sources (Figure S8). For the 7-factor solution, the model predicted concentrations of tracers such as Ca, V, NH_4^+, and NO_3^- correlated with the observed values with coefficients of determination R^2 of 0.92, 0.91, 0.98, and 0.88, respectively (Table S4).

The high R^2 values of bulk species indicate that the 7-factor model fits well for the data. For tracers like Si, Mn, Se, and Cu, the scaled residuals follow a normal distribution with a mean of 0 and a variance of 1. For bulk species like NH_4^+, NO_3^-, and SO_4^{2-}, the scaled residuals exhibit a light-tailed distribution, with the highest frequency concentrated near 0 and ranging from -2 to 2. Additionally, the scaled residuals of the bulk species OC and EC follow a normal distribution with a mean of 0 and a variance of 1. The distribution of scaled residuals demonstrates the validity of our solution. Physically, the 7-factor solution successfully decouples all distinct emission sources without redundant splitting."

Comment #5:

An important contribution of the study is not only that PMFr often performs well numerically, but also that it preserves source-related structure in a way that may be more physically meaningful for subsequent source apportionment. At present, however, these two strengths are sometimes discussed together as if they were the same claim.

The paper would be stronger if it clearly distinguished between them. For example, there may be situations in which another method performs competitively on certain numerical metrics, whereas PMFr retains greater interpretive consistency in the source-apportionment context. Making this distinction explicit would sharpen the central message of the paper.

Response:

Indeed, numerical imputation accuracy and preservation of source-related structure are two distinct aspects of PMFr and should be clarified. Numerical metrics such as R^2, IoA, and MAPE evaluate concentration-level reconstruction accuracy, whereas source-structure preservation evaluates whether the completed dataset remains suitable for physically interpretable PMF source apportionment.

To address this issue, we revised the manuscript to define two complementary validation endpoints: direct reconstruction accuracy and physical source-feature preservation. We further added a subsequent PMF evaluation to explicitly assess the second endpoint. Two representative cases were selected for this analysis: SO_4^{2-} missingness in Case 2 and high-concentration Fe missingness in Case 5. These cases were chosen because the numerical advantage of PMFr over baseline methods became less substantial, allowing us to test whether PMFr could still retain greater interpretive consistency in downstream PMF analysis under such narrowed performance gaps.

The results showed that PMFr better preserved the source-profile composition of the secondary sulfate and crustal dust factors, including the SO_4^{2-}/ NH_4^+, Fe/Ca, and Ca/Si relationships, and achieved the highest agreement with the complete-dataset source contributions. PMFr also more consistently reproduced the temporal features of these sources, including daytime SS enhancement and CD peaks associated with daytime dust-related activities. This clarification sharpens the central message that PMFr is valuable not only because it reconstructs missing concentrations accurately, but also because it better preserves source-related chemical and temporal structures required for subsequent PMF analysis.

Revised Section 3.3 "Assessing the Impact of Imputation on PMF Source Apportionment" as below (Line 260-290):

"Results showed that the advantage of PMFr over baseline methods narrowed mainly under two challenging conditions: instrument-failure-type missingness and missingness of specific species such as SO_4^{2-} and crustal elements such as Fe. Accordingly, two representative cases were selected for downstream PMF evaluation: SO_4^{2-} missingness in Case 2 at a 10% missing rate and high-concentration Fe missingness in Case 5 at a 20% missing rate. The SS and CD factors were used to assess whether these imputation differences propagated into PMF-resolved source profiles and source contributions. For the SS factor (Figure S32), the SO_4^{2-}/ NH_4^+ mass ratio derived from the PMFr-completed dataset was 3.39 (NH_4^+ associated with NH_4NO_3 removed), close to that from the complete observed dataset (3.44). BPCA also produced a comparable ratio of 3.33, whereas LI (3.93), KNN (2.91), DBN (2.55), and Mean (3.83) showed larger deviations. This indicates that PMFr better preserved the SO_4^{2-}- NH_4^+ relationship in the SS profile, which is critical for maintaining the chemical interpretability of the SS factor. For the CD factor (Figure S33), PMFr also reproduced the crustal elemental ratios consistently. The Fe/Ca and Ca/Si ratios from the complete observed dataset were 0.93 and 1.64, respectively, while PMFr yielded corresponding values of 0.95 and 1.62. In contrast, larger deviations were observed for several baseline methods, such as DBN for Fe/Ca (1.21) and BPCA or LI for Ca/Si (1.43 and 1.44, respectively). These results suggest that inappropriate imputation can alter the resolved source-profile composition, whereas PMFr maintains the physical consistency of source profiles.

For the SS factor contributions, PMFr achieved the highest Pearson's correlation coefficient (r) of 0.943, followed by KNN (0.914), BPCA (0.913), LI (0.900), Mean (0.802), and DBN (0.743). For the CD factor contributions, PMFr also showed the highest temporal agreement, with an r of 0.954, followed by Mean (0.948), KNN (0.926), BPCA (0.925), LI (0.796), and DBN (0.706). These results indicate that competitive concentration-level imputation does not necessarily guarantee equivalent preservation of PMF-resolved source-contribution patterns.

As shown in Figure S34a,b, the PMFr-derived SS contribution closely reproduced the diurnal pattern from the original complete dataset, particularly during daytime periods when secondary sulfate formation is expected to be enhanced. Similarly, PMFr captured the diurnal variation of CD more consistently than baseline methods, especially around the daytime peak likely associated with dust resuspension and other daytime dust-related activities. The selected time-series episodes showed the same behavior (Figure S35a,b). For Case 2 at a 20% missing rate, PMFr achieved the highest r of 0.985 for SS, compared with BPCA (0.981), KNN (0.980), DBN (0.954), LI (0.936), and Mean (0.705). For the high-Fe missing case, PMFr also showed the highest agreement for CD, with an r of 0.951, followed by Mean (0.928), BPCA (0.888), KNN (0.881), DBN (0.713), and LI (0.683). Therefore, the advantage of PMFr is not limited to pointwise concentration accuracy; it also better preserves the chemical and temporal source structures needed for physically interpretable PMF source apportionment. These results indicate that inaccurate imputation may propagate into PMF analysis and introduce source-apportionment biases, potentially making the imputed dataset less reliable than one processed using conventional PMF missing-value treatments."

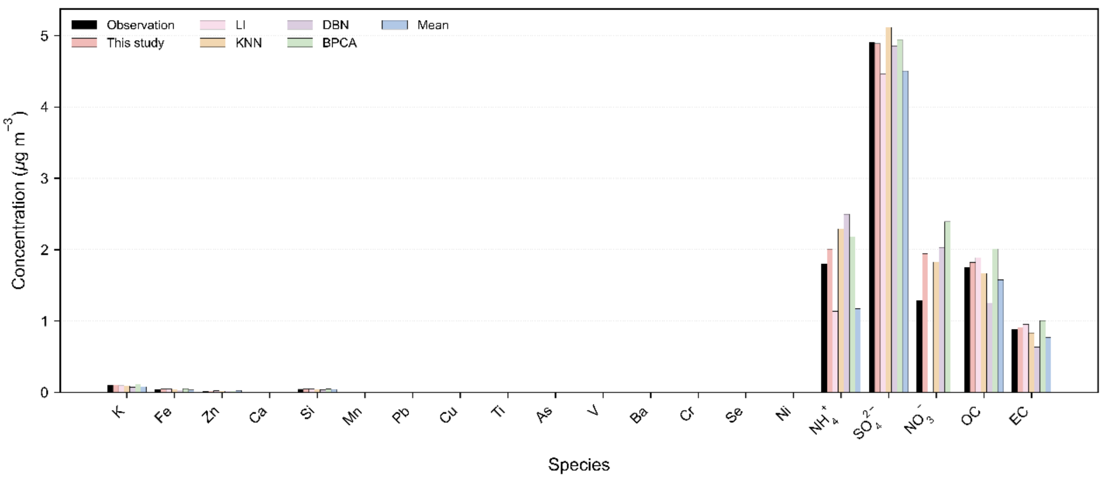


Figure S32. Comparison of PMF-resolved secondary sulfate source profiles derived from datasets completed using different imputation methods and from the complete non-missing dataset under Case 2.

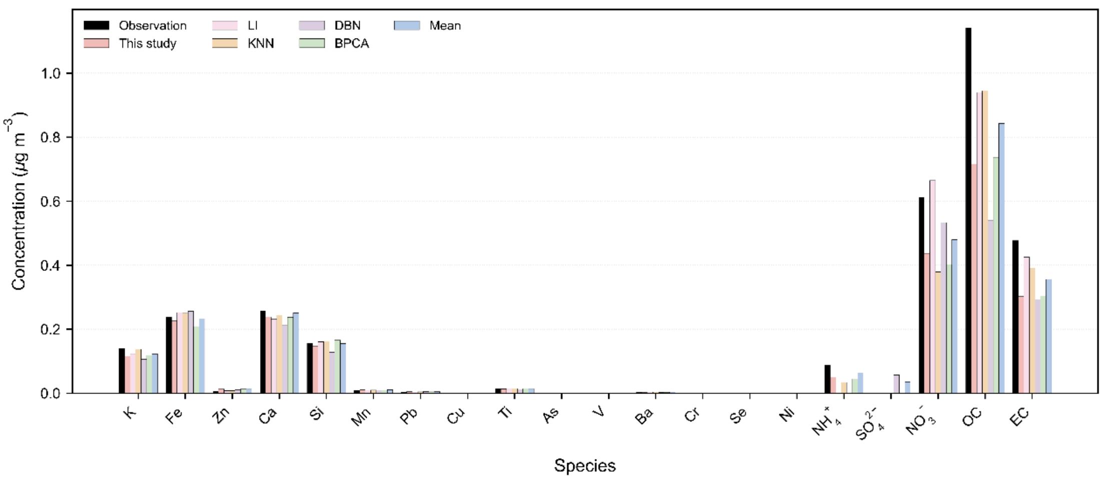


Figure S33. Comparison of PMF-resolved crustal dust source profiles derived from datasets completed using different imputation methods and from the complete non-missing dataset under Case 5.

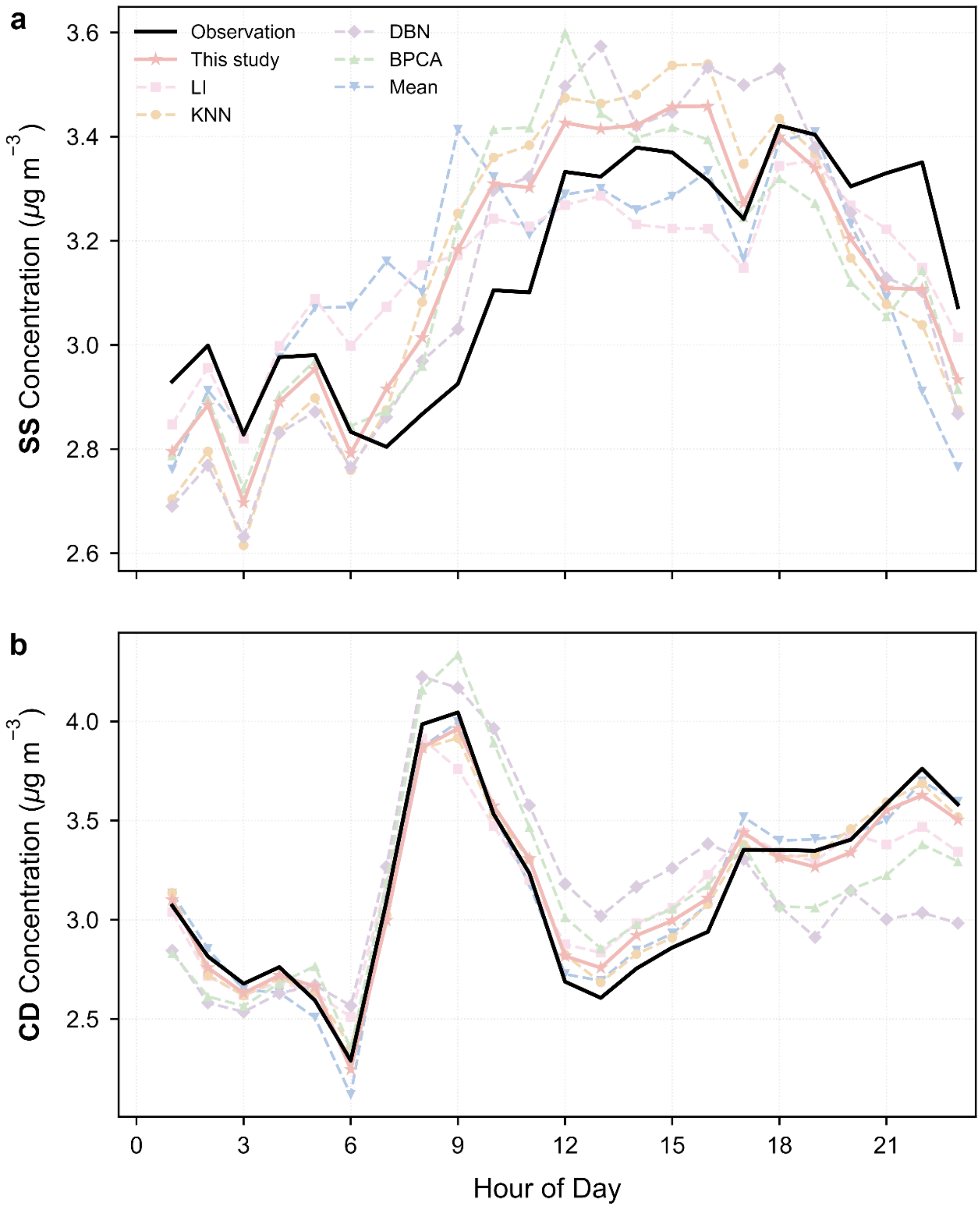
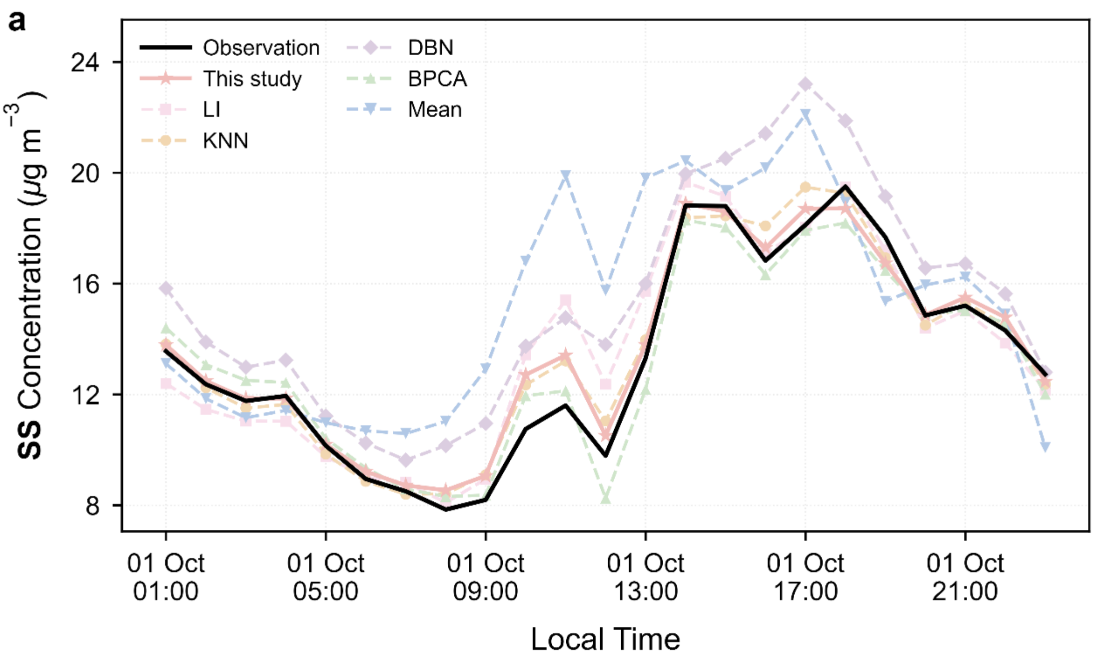


Figure S34. Diurnal variations of PMF-resolved source contributions after imputation for representative cases: **(a)** secondary sulfate (SS) contribution under Case 2 and **(b)** crustal dust (CD) contribution in Case 5.



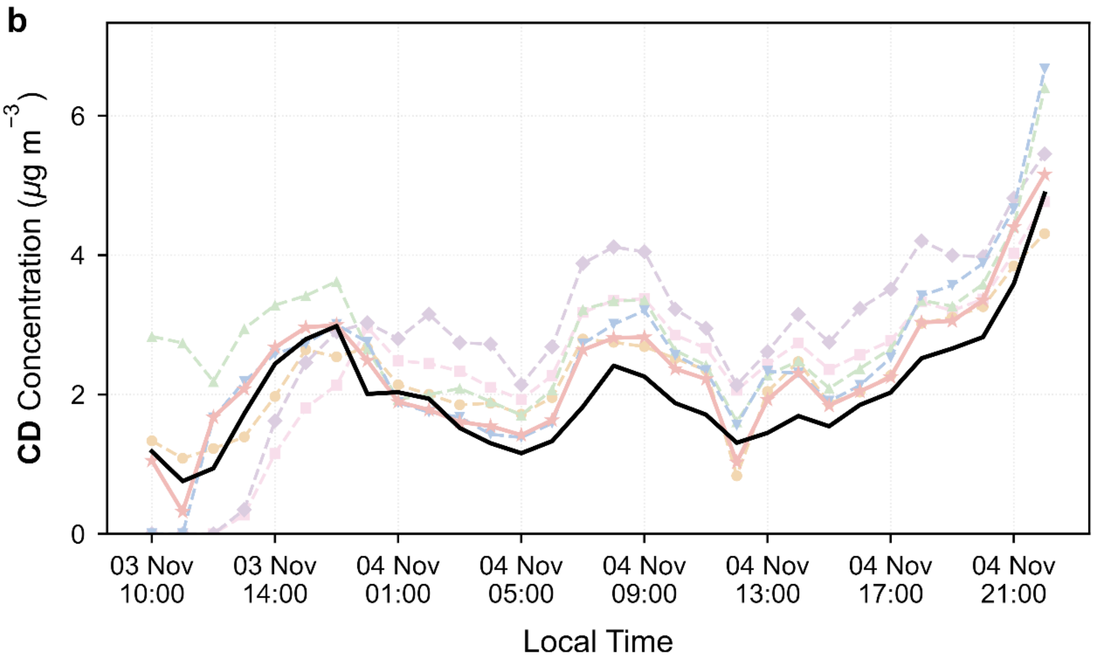


Figure S35. Selected time-series episodes of PMF-resolved source contributions after imputation: **(a)** secondary sulfate (SS) contribution under Case 2 and **(b)** crustal dust (CD) contribution under Case 5.

Minor Comments:

Comment #1:

The manuscript contains a number of grammatical and stylistic issues, including subject-verb agreement errors, awkward phrasing, incorrect verb forms, article usage problems, and inconsistent spacing around parentheses.

(e.g., "by multipling", "The best-fitting solution were selected", "Potassium (K) was treat as missing", "PMFr achieve/decline/capture", and "~of scaled residuals (Reff et al., 2007;~")

Response:

We sincerely apologize for the grammatical and stylistic errors in the original manuscript. We have performed a comprehensive professional proofreading of the entire text to ensure clarity and technical accuracy.

1. Changed "by multipling the estimated source-specific $PM_{2.5}$ mass" to "by multiplying the estimated source-specific $PM_{2.5}$ mass by the resolved source profiles." **(Line 45-46)**
2. Changed "Potassium (K) was treat as missing" to "Potassium (K) was treated as missing." **(Line 94)**
3. Changed "distributions of scaled residuals(Reff et al., 2007; Brown et al., 2015)" to "distributions of scaled residuals (Reff et al., 2007; Brown et al., 2015)" **(Line 133)**
4. Changed "both with low standard deviation" to "both with low standard deviations." **(Line 180-181)**
5. Changed "The best-fitting solution were selected" to "The best-fitting solution was selected." **(Line 131-132)**
6. Changed "with DBN exhibiting lower standard deviation" to "with DBN exhibiting a lower standard deviation." **(Line 181)**
7. Changed "according to the trend indicator R^2, 0.96 and 0.91, respectively." to "For inorganic ions, PMFr performs best when imputing NH_4^+ and NO_3^- with R^2 values of 0.96 and 0.91, respectively." **(Line 182)**
8. Changed "The performance of PMFr decline" to "The performance of PMFr declines." **(Line 184)**
9. Changed "Nevertheless PMFr still outperforms" to "Nevertheless, PMFr still outperforms." **(Line 185)**
10. Changed "struggle to impute high SO_4^2- concentrations accurately." to "struggle to accurately impute high SO_4^2- concentrations." **(Line 188)**
11. Changed "typically dominates nitrate" to "typically dominates the nitrate fraction." **(Line 190)**
12. Changed "but also higher MAPE" to "but also a higher MAPE." **(Line 193)**
13. Changed "element concentration fluctuates" to "element concentrations fluctuate." **(Line 196-197)**
14. Changed "missing data(Junninen et al., 2004)" to "missing data (Junninen et al., 2004)." **(Line 202-203)**
15. Changed "caused by random missing." to "caused by random missingness." **(Line 208)**

16. Changed “when the missing percentage are 10% and 20%” to “when the missing percentages are 10% and 20%.” **(Line 213-214)**
17. Changed “owing to constructed source-receptor relationships” to “owing to the constructed source-receptor relationships.” **(Line 216-217)**
18. Changed “the difficulty machine-learning methods face” to “the difficulties that machine-learning methods face.” **(Line 217)**
19. Changed “shows best agreement” to “shows the best agreement.” **(Line 209)**
20. Changed “PMFr capture the temporal variability” to “PMFr captures the temporal variability.” **(Line 228-229)**
21. Changed “under Case 6-8” to “under Cases 6-8.” **(Line 236-237)**
22. Changed “the degradation being substantial in Case 6” to “with the degradation being substantial in Case 6.” **(Line 241-242)**
23. Changed “proved by Lee et al. (Lee et al., 2023)” to “have also been reported by Lee et al. (2023)” **(Line 254)**

Comment #2:
Table 1 should be checked for ion notation consistency. Several ionic species are listed without charge notation (e.g., NH_4, SO_4, NO_3, Ca, K), whereas the main text uses formal ionic expressions.

Response: Modified.

Comment #3:
The conclusion section does a good job of emphasizing the promise of PMFr, but it would be stronger if it also briefly acknowledged the conditions under which the method appears less robust. A short, balanced statement about both the advantages and the observed limitations would make the paper’s ending more convincing and scientifically grounded.

Response:
We appreciate the reviewer’s valuable suggestion, which helped us make the Conclusion section more balanced and scientifically grounded. To address this comment, we revised the Conclusion section to include a balanced statement on the observed limitations of PMFr. Specifically, we now state that the advantage of PMFr may become less substantial when source-related constraints are weakened, such as when all key tracers for a specific source factor are simultaneously missing, or when baseline methods can already capture stable co-variation patterns for certain species. We also added that the chemically consistent and physically meaningful estimates

produced by PMFr rely on the temporal stability of source chemical compositions, and that source stability should be verified before applying PMFr to long-term datasets.

The revised Conclusion now reads (Line 330-341):

"We developed a physically interpretable imputation method (PMFr) for reconstructing missing $PM_{2.5}$ speciation data by leveraging source--receptor relationships encoded in key chemical species. Benchmarking against commonly used imputation techniques, including Mean, LI, KNN, BPCA, and a deep learning predictive model, demonstrates that PMFr achieves improved accuracy and robustness while preserving physical and chemical interpretability, especially for key marker species. Crucially, the PMFr-completed dataset is better suited for subsequent PMF source apportionment because it preserves source-profile composition and source-contribution temporal features. Nevertheless, the advantage of PMFr may become less substantial when source-related constraints are weakened, such as when all key tracers for a specific source factor are simultaneously missing, or when baseline methods can already capture stable co-variation patterns for certain species. These chemically consistent and physically meaningful estimates also rely on the temporal stability of source chemical compositions. Recognizing the limitations of such static assumptions for long-term datasets, we highlight the necessity of systematically verifying source stability in extended applications. Therefore, this work offers a simple and generalizable solution that strengthens the reliability of real-world speciation datasets and enhances their suitability for source apportionment and policy-relevant analyses."

Reviewer #3

This manuscript proposes a novel imputation framework (PMFr) that leverages source–receptor relationships derived from PMF to reconstruct missing $PM_{2.5}$ speciation data. Addressing missing data due to instrument failures and monitoring gaps is an important and practical issue, and the attempt to incorporate physically interpretable source profiles rather than relying solely on statistical covariance is a clear strength of this work.

However, several key aspects of the methodology require further elaboration. In particular, the role of the pre-imputation step, the justification for the assignment of uncertainties, and the comparison with standard PMF practices need to be addressed to fully demonstrate the robustness of the proposed approach. I recommend major revisions to clarify the workflow and to more rigorously validate the method before the manuscript can be considered for publication.

Major Comments:

Comment #1:

The methodological description in Section 2.3 would benefit from further clarification to address potential concerns about model independence. According to the text, tracer species are first imputed using another method, such as KNN, while non-tracers are filled using the geometric mean prior to the initial PMF run. Given that the PMFr framework relies on these pre-imputed values to derive source profiles and subsequently reconstruct missing data, it is currently difficult to isolate the performance of the PMFr method itself from the accuracy of the initial KNN imputation. To address this, the authors should clearly delineate the full workflow, including all intermediate steps. Providing a comprehensive flowchart in Figure 1 that details the full pipeline from raw data to pre-imputation, initial PMF, reconstruction, and the final PMF would greatly improve clarity. Additionally, conducting a sensitivity analysis to evaluate how different pre-imputation methods in pre-imputed tracers propagate into the final PMFr results is necessary to demonstrate the methodological robustness of the framework.

Response:

We sincerely thank the reviewer for this valuable suggestion. To address this concern, we revised Section 2.3 (Line 98-122) and updated Figure 1 to show the complete PMFr workflow, including raw data preprocessing, source identification (initial PMF run), pre-imputation, PMF-based reconstruction using the $G \times F$ structure, and validation.

In addition, we added a sensitivity analysis of the first pre-imputation step in Text S5 and Table S14. Different algorithms, including LI, KNN, DBN, and BPCA, were used for the initial pre-imputation step, and the final PMFr reconstruction results were compared. The results show that PMFr remains relatively stable across different pre-imputation methods. For NH_4^+, the final PMFr R^2 values range from 0.92 to 0.96 and the MAPE values range from 20.67% to 24.58%. For NO_3^-, the final PMFr R^2 values range from 0.85 to 0.90, while the MAPE values range from 22.91% to 33.11%.

These results indicate that the final PMFr reconstruction is not simply determined by the initial KNN imputation. Although an initial estimate is required, PMFr refines the reconstructed values through PMF-resolved source profiles and source-receptor constraints.

Our revisions have been added in Section 2.3, Figure 1, Text S5, and Table S14.

1. Revised Section 2.3 text (Line 98-122):

"A tracer for imputation, hereafter referred to as a tracer, is defined as a key species that distinguishes a specific factor from others and reflects how that factor influences the receptor over time. Co-tracers refer to co-varying tracers within the same factor, collectively characterizing the temporal behavior of the corresponding source. As illustrated in Figure 1, PMF is first applied to resolve factor profiles and their contributions, providing source--receptor relationships constrained by expert knowledge, given that pollution sources imprint distinct temporal patterns on the receptor. Details of the usage of PMF for SA can be found in the literature, and the uncertainty settings are provided in Text S3. Based on the SA results with selected source profiles, species requiring imputation are classified as tracers or non-tracers through a knowledge-driven step.

When imputing tracers, the availability of co-tracers should be checked at each timestamp before reconstruction, because the source contribution vector G needs to be constrained by source-specific tracer information. If all tracers associated with a specific factor are simultaneously missing, the corresponding G vector is less directly constrained by observed species; in such cases, these missing tracer values are first imputed using another imputation method, with KNN recommended for its simplicity, efficiency, and ability to provide a reasonable estimate of temporal variation. The corresponding uncertainty is set to 10% of the imputed concentration. For missing tracers with available co-tracers, as well as for non-tracers, missing values are replaced by the geometric mean. The uncertainty calculation is further discussed in Text S4.

The pre-imputed dataset and its associated uncertainty matrix are then input into the PMF model for reconstruction. The PMF run decomposes the dataset into factor profiles (F) and source contributions (G), and data reconstruction is achieved by multiplying the G and F matrices. Rather than relying directly on covariance in the high-dimensional chemical dataset, PMFr reconstructs missing values within this low-entropy source structure represented by PMF-resolved source profiles and temporal contributions.

The performance of PMFr was evaluated using two complementary validation endpoints: direct reconstruction accuracy and physical source-feature preservation. The reconstructed concentrations were directly compared with observed values and benchmarked against baseline methods, including LI, KNN, DBN, BPCA, and geometric mean imputation (Mean), using R^2, IoA, and MAPE. The U.S. EPA PMF 5.0 User Guide recommends handling missing values by replacing them with the species median and assigning a high uncertainty to downweight these substituted values. Here, missing values were replaced by the species-specific geometric mean, following the same constant-substitution and downweighting principle. Because the geometric mean is also a robust central value for skewed data and was adopted in the previous PMF analysis using the same hourly $PM_{2.5}$ speciation dataset, it was used here as a representative conventional PMF missing-value treatment for comparison with PMFr. Physical source-feature preservation was further assessed by comparing the PMF-resolved source profiles and corresponding source contributions obtained from different imputed datasets with those derived from the original complete dataset.

2. Revised Figure 1:

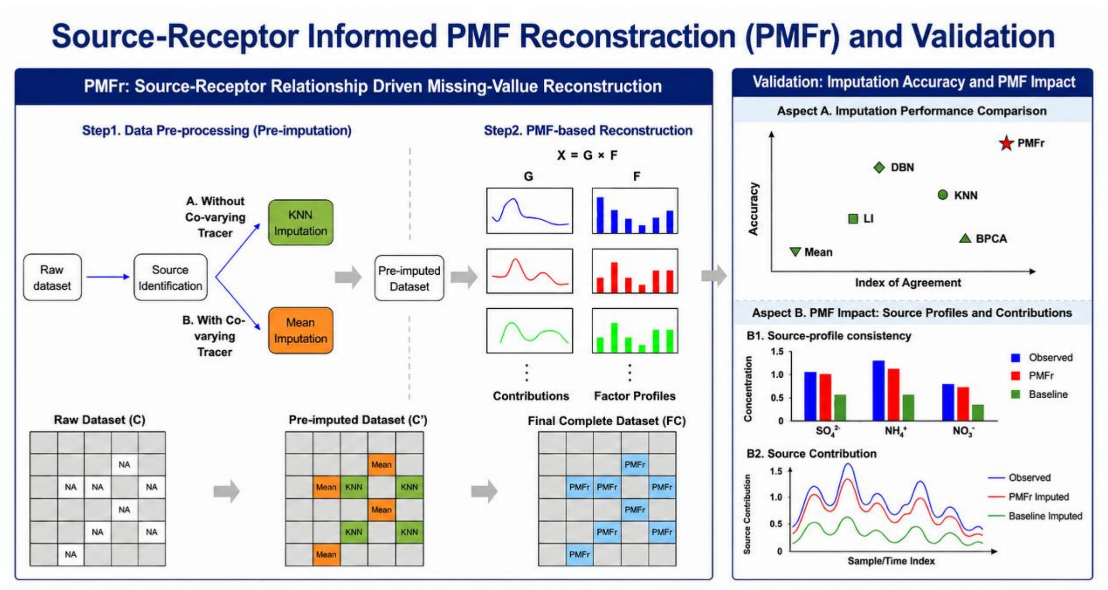


Figure 1. Flow chart of Source-Receptor Informed Positive Matrix Factorization Reconstruction (PMFr) and validation.

3. Added Text S5: Sensitivity Analysis of the First Pre-imputation Step

“Sensitivity analysis was conducted to quantify the impact of the pre-imputation step. As shown in Table S14, the final PMFr reconstruction metrics vary depending on the initial pre-imputation algorithm. For NH_4^+, utilizing KNN as the pre-imputation method yields an R^2 of 0.92, an IoA of 0.95, and a MAPE of 20.67%. DBN results in an R^2 of

0.95, an IoA of 0.92, and a MAPE of 23.61%. BPCA produces an R^2 of 0.96, an IoA of 0.81, and a MAPE of 24.58%. Across the tested algorithms for NH_4^+, the R^2 values range from 0.92 to 0.96, and the MAPE ranges from 20.67% to 24.58%. For NO_3^-, KNN achieves an R^2 of 0.85, an IoA of 0.95, and a MAPE of 23.92%. DBN yields an R^2 of 0.89, an IoA of 0.91, and a MAPE of 33.11%. BPCA results in an R^2 of 0.90, an IoA of 0.75, and a MAPE of 22.91%. For NO_3^-, the resulting R^2 values range from 0.85 to 0.90, while the MAPE spans from 22.91% to 33.11%. These results suggest that the PMFr maintains robust imputation performance regardless of the specific pre-imputation algorithm applied. Although the initial step is required, the PMFr method yields better performances than the baseline KNN approach. For NH_4^+ under MCMS, the PMFr MAPE is 20.67% versus the KNN MAPE of 24.00% at a 10% missing rate, and 25.87% versus 45.33% at a 20% missing rate. This improvement is achieved because subsequent PMF iterations impose source-profile constraints on the reconstructed values, such as maintaining a NO_3^-/NH_4^+ mass ratio of approximately 3 for the SN factor."

4. Added Table S14:

Table S14. Sensitivity analysis of different pre-imputation methods under the MCMS mechanism (Case 4, 10% missing rate)

Species	Pre-Imputation Method	R^2	IoA	MAPE(%)
NH_4^+	KNN	0.92	0.95	20.67
	LI	0.82	0.88	40.32
	DBN	0.95	0.92	23.61
	BPCA	0.96	0.81	24.58
NO_3^-	KNN	0.85	0.95	23.92
	LI	0.76	0.90	42.04
	DBN	0.89	0.91	33.11
	BPCA	0.90	0.75	22.91

Comment #2:

While the manuscript comprehensively compares PMFr against LI, KNN, BPCA, and DBN, it omits the most widely used baseline in receptor modeling practice. The U.S. EPA PMF 5.0 User Guide recommends handling missing values by replacing them with the species median and assigning an uncertainty of four times the median (400%). As this approach is routinely used in real-world PMF applications, including it as a baseline would help the receptor modeling community better assess the meaningful improvement provided by PMFr. The authors are encouraged to include this EPA-recommended method as a baseline and compare the PMFr performance against it under the various missing-data scenarios.

Response:

We thank the reviewer for this valuable suggestion from the perspective of source apportionment practice. The U.S. EPA PMF 5.0 User Guide recommends replacing missing values with the species median, while foundational PMF studies have also used geometric mean substitution; both approaches follow the same principle of replacing missing values with a robust central value and assigning a high uncertainty to reduce the influence of outliers and limit the impact of substituted values on model fitting (Norris et al., 2014; Polissar et al., 1994). In this study, geometric mean imputation was used as a representative conventional PMF missing-value treatment because the geometric mean is also a robust central value for skewed data and was adopted in our previous PMF analysis using the same hourly $PM_{2.5}$ speciation dataset. To make this rationale clearer, we have added an explicit explanation in **Section 2.3 (Line 121-126)**. Our quantitative evaluation shows that geometric mean imputation yields an overall MAPE of 66.75%. Because this approach replaces missing data with a constant value, it exhibits no temporal variation. This inherent structural limitation prevents it from capturing the dynamic fluctuations of pollutant concentrations, resulting in high absolute errors across the individual missing-data scenarios, as shown in Figures S11--S29. We have added **Section 3.2.1 (169-178)** to include the quantitative comparison for the geometric mean imputation method. Furthermore, we added a rationale stating that, given its lack of temporal variation, as shown across all individual scenarios in Figures S11--S29, and its high overall MAPE, its performance is quantified solely in this overall assessment and is excluded from further detailed trend comparisons in subsequent sections. In addition, the conventional geometric mean imputation method was included in the subsequent PMF analysis to evaluate its influence on PMF-resolved source profiles and source contributions (Lines 254-284).

The revised text in Section 2.3 and Section 3.2.1 is as follows:

1. Revised text in Section 2.3 (Line 121-126):

The U.S. EPA PMF 5.0 User Guide recommends handling missing values by replacing them with the species median and assigning a high uncertainty to downweight these substituted values. Here, missing values were replaced by the species-specific geometric mean, following the same constant-substitution and downweighting principle. Because the geometric mean is also a robust central value for skewed data and was adopted in the previous PMF analysis using the same hourly $PM_{2.5}$ speciation dataset, it was used here as a representative conventional PMF missing-value treatment for comparison with PMFr.

2. Revised text in Section 3.2.1 (Line 169-178)

"For simple baseline methods, LI produces an R^2 of 0.35 and a high MAPE of 61.7%, while the geometric mean imputation method (Mean) results in a higher MAPE of 66.75%. Given that mean imputation produces a constant value without temporal variation and consistently fails to provide effective reconstruction across individual scenarios (Figures S11-S29), its performance is solely quantified by MAPE here and is excluded from further detailed comparisons in subsequent sections."

Reference:

Norris, G., Duvall, R., Brown, S., & Bai, S. (2014). *EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide* (EPA/600/R-14/108). U.S. Environmental Protection Agency, Washington, DC.

Polissar, A. V., Hopke, P. K., Paatero, P., Malm, W. C., & Sisler, J. F. (1998). Atmospheric aerosol over Alaska: 2. Elemental composition and sources. *Journal of Geophysical Research: Atmospheres*, 103(D15), 19045-19057. https://doi.org/10.1029/98JD01212

Xie, M., Lu, X., Ding, F., Cui, W., Zhang, Y., and Feng, W.: Evaluating the influence of constant source profile presumption on PMF analysis of $PM_{2.5}$ by comparing long- and short-term hourly observation-based modeling, Environmental Pollution, 314, 120273, https://doi.org/10.1016/j.envpol.2022.120273, 2022.

Comment #3:

The treatment of uncertainty in Section 2.3 requires further justification. The manuscript states that tracers are assigned an uncertainty equal to 10% of their imputed value, while non-tracers are assigned an uncertainty equal to eight times the geometric mean. The physical or statistical rationale for these specific multipliers is currently missing. Since the uncertainty matrix directly controls the PMF objective function (Q-value) and strongly influences the model solution, these parameters are critical. The authors should provide a justification for these choices, whether through literature references, empirical evidence, or theoretical reasoning, and briefly discuss or conduct a sensitivity analysis demonstrating how different uncertainty assignments might affect the PMFr performance and subsequent PMF outputs.

Response:

To address this concern, we added Text S4, "Discussion on Data Treatment of PMFr Uncertainty", to explain the rationale for assigning different uncertainties to pre-imputed tracers, geometrically filled tracers, and non-tracers.

For missing tracers without available co-tracers, the corresponding G vector is less directly constrained by observed species. Therefore, these missing tracer values are first estimated using another imputation method, with KNN recommended for its simplicity, efficiency, and ability to provide a reasonable estimate of temporal variation. Their uncertainty is set to 10% of the imputed concentration so that these pre-imputed tracer values retain sufficient statistical weight in the PMF calculation and can provide source-specific temporal information for constraining G, rather than being effectively ignored during factorization. This setting is supported by previous PMF analysis using the same observation site and hourly $PM_{2.5}$ speciation dataset (Xie et al., 2022).

For missing tracers with available co-tracers and for non-tracers, the imputed values are not intended to provide the primary temporal constraint because available co-tracers or other observed species already provide stronger information for resolving G. Therefore, these values are assigned a much larger uncertainty, defined as eight times the geometric mean. Standard receptor-modeling practice commonly assigns missing data an uncertainty of four times the geometric mean concentration (Polissar et al., 1994). In this study, we further tested larger multipliers and selected eight times the geometric mean because it provided an appropriate balance: it sufficiently downweighted these geometrically filled values while maintaining stable PMF reconstruction. This treatment minimizes the influence of potentially biased geometric-mean substitutions on the Q-value objective function and ensures that the PMF solution is primarily driven by reliable observed species and available source-related tracers.

Text S4. Discussion on Data Treatment of PMFr Uncertainty

"The uncertainty matrix directly determines the statistical weight of individual data points in the Positive Matrix Factorization (PMF) objective function (Q). In PMFr, uncertainty assignment is designed according to the role of each filled value in constraining the source contribution matrix (G). Specifically, when imputing tracers, the availability of co-tracers should first be checked at each timestamp because G needs to be constrained by source-specific tracer information.

If all tracers associated with a specific factor are simultaneously missing, the corresponding G vector is less directly constrained by observed species. In such cases, the missing tracer values are first estimated using another imputation method, with KNN recommended for its simplicity, efficiency, and ability to provide a reasonable estimate of temporal variation. The corresponding uncertainty is set to 10% of the imputed concentration. This uncertainty setting allows the pre-imputed tracer values to retain sufficient statistical weight in the PMF calculation, so that they can provide source-specific temporal information for constraining G, rather than being effectively ignored during factorization. This setting is supported by previous PMF analysis using the same observation site hourly $PM_{2.5}$ speciation dataset. For missing tracers with available co-tracers, as well as for non-tracers, missing values are replaced by the species-specific geometric mean. In these cases, the filled values are not intended to provide the primary temporal constraint for the corresponding source factor, because available co-tracers or other observed species already provide stronger information for resolving G. Therefore, these filled values are assigned a much larger uncertainty, defined as eight times the geometric mean. Standard receptor-modeling practice commonly assigns missing data an uncertainty of four times the median or geometric mean concentration. Here, a larger multiplier was adopted to more strongly downweight these filled values. This treatment minimizes the influence of potentially biased geometric mean substitutions on the Q -value objective function and ensures that the PMF solution is primarily driven by reliable observed species and available source-related tracers."

Reference:

Xie, M., Lu, X., Ding, F., Cui, W., Zhang, Y., and Feng, W.: Evaluating the influence of constant source profile presumption on PMF analysis of $PM_{2.5}$ by comparing long- and short-term hourly observation-based modeling, Environmental Pollution, 314, 120273, https://doi.org/10.1016/j.envpol.2022.120273, 2022.

Polissar, A. V., Hopke, P. K., Paatero, P., Malm, W. C., & Sisler, J. F. (1998). Atmospheric aerosol over Alaska: 2. Elemental composition and sources. *Journal of Geophysical Research: Atmospheres*, 103(D15), 19045-19057. https://doi.org/10.1029/98JD01212