Responses to the comments from the editor and the reviewers

Manuscript ID: EGUSPHERE-2026-2447

Original Title: " Mass-constrained source apportionment of nitrate-containing particles in eastern China using a SPAMS-NMF framework "

Revised Title: " Mass-constrained characterization of nitrate-containing particles in eastern China using single-particle aerosol mass spectrometry "

CC#1

The manuscript presents a study on winter nitrate-containing particles in eastern China using a semi-quantitative SPAMS–NMF framework. The authors conducted autumn–winter observations at the Dianshan Lake Atmospheric Superstation near Shanghai and combined single-particle aerosol mass spectrometry with bulk measurements, meteorology, and non-negative matrix factorization to identify nitrate-containing particle classes and source contributions. The study finds that nitrate-containing particles were mainly in the accumulation mode around 0.5–0.7 μm, with the aged NO_3Lv4 class dominating both particle number and nitrate mass contribution. The manuscript is relevant to winter haze formation, nitrate aerosol chemistry, and source apportionment in the Yangtze River Delta.

1. The manuscript should more clearly explain the novelty of the proposed SPAMS–NMF framework. The authors state that the method is mass-constrained and semi-quantitative, but it would be helpful to clarify how this approach improves upon previous SPAMS-based source apportionment studies and what the main methodological advancement is.

- Thank you for this important comment. In the revised manuscript, we have clarified that the principal methodological advancement of this study is not the application of NMF itself, but the development of a mass-constrained semi-quantitative framework that links particle-resolved SPAMS information with independently measured bulk nitrate mass.

Conventional SPAMS measurements primarily provide particle counts, relative

ion intensities, chemical signatures, and mixing-state information, but do not directly provide species-resolved absolute mass concentrations. In our framework, bulk nitrate measured by MARGA is used as an external mass constraint, and SPAMS-derived nitrate-related signals and particle information are subsequently used to estimate the particulate nitrate mass associated with different particle classes and subclasses. This allows the particle-resolved chemical information obtained from SPAMS to be interpreted on a nitrate-mass-relevant basis rather than solely in terms of particle number or relative ion intensity.

We have also clarified the role of NMF in the revised manuscript. NMF is no longer presented as the central novelty or as an additional particle-classification scheme. Instead, it is applied to the temporally resolved, semi-quantified particulate nitrate contributions to provide complementary source- and process-related context. Thus, the main methodological contribution is the bridge between particle-resolved chemical characterization and bulk nitrate mass constraints, while NMF provides an additional temporal interpretation of the resulting particle-resolved nitrate information.

2. The regression-based conversion from SPAMS particle information to nitrate mass concentration needs further justification. The reported correlation coefficient of the MLR model is moderate, and the authors should discuss the uncertainty this introduces into the subsequent NMF source apportionment and particle-class mass estimates.

- We appreciate your valuable comments. We agree that the moderate correlation of the MLR model (R = 0.68) requires explicit consideration when interpreting the subsequent particle-class nitrate mass estimates and NMF results.

The regression model is used as an empirical mass-constrained correction rather than as an exact physical conversion or mechanistic model. We have therefore expanded the uncertainty discussion to clarify that the remaining unexplained variance mainly introduces uncertainty into the absolute magnitude of the estimated particulate nitrate mass. Consequently, class- and subclass-resolved nitrate mass contributions should be interpreted as semi-quantitative estimates rather than exact quantitative values.

Because the same mass-constrained procedure and allocation scheme are applied

consistently across all particle populations, relative differences among the dominant particle classes and their temporal variations are expected to be more robust than their absolute mass values. We have also clarified that low-abundance subclasses may have greater relative uncertainty because they are more sensitive to particle-counting statistics and classification errors.

Importantly, the NMF analysis inherits uncertainty from the semi-quantitative input matrix. Therefore, the NMF factors are interpreted conservatively using multiple lines of evidence, including factor profiles, temporal and diurnal behavior, SPAMS chemical characteristics, and independent bulk chemical tracers, rather than relying solely on the absolute magnitude of the semi-quantified nitrate mass. These limitations have been explicitly incorporated into the revised Supplement and the Conclusions and Atmospheric Implications section.

3. The interpretation of the four nitrate-containing particle classes should be made more concise and transparent. The transition from NO_3Lv1 to NO_3Lv4 is described as increasing nitrate enrichment and aging, but the criteria used to distinguish these classes should be summarized more clearly for readers who are less familiar with SPAMS spectral classification.

- Thank you for this helpful comment. We agree that the original interpretation of NO3Lv1–NO3Lv4 as a progressive nitrate-enrichment or aging sequence was too strong and could be misleading. We have therefore substantially revised this interpretation.

In the revised manuscript, NO3Lv1–NO3Lv4 are no longer described as sequential stages of nitrate enrichment or atmospheric aging. Instead, they are interpreted as four recurrent nitrate-containing particle populations distinguished primarily by their mass-spectral characteristics and temporal behavior. The averaged spectra show two broad chemical relationships: NO3Lv1 and NO3Lv2 exhibit relatively stronger sulfate-related signals and weaker nitrate-related signals, whereas NO3Lv3 and NO3Lv4 show enhanced nitrate fragments, particularly NO_2^- and NO_3^-, together with comparatively weaker sulfate signals. Thus, NO3Lv1–NO3Lv2 and NO3Lv3–NO3Lv4 are treated as two chemically related pairs.

We further show that all four classes have broadly similar accumulation-mode vacuum aerodynamic size distributions, with modal Dva values near 0.6 μm, whereas their diurnal patterns differ substantially. Particle size is therefore treated as a supporting characteristic rather than as evidence for a progressive aging sequence. The revised description provides a more transparent basis for the four-class framework by emphasizing the combined spectral and temporal characteristics used to distinguish the particle populations.

4. The discussion of nocturnal heterogeneous nitrate formation should be expressed more cautiously. Since NO_3, N_2O_5, and $ClNO_2$ were not directly measured, the authors should clearly distinguish between direct observational evidence and inferred mechanisms based on nighttime enhancement, high relative humidity, and stagnant boundary-layer conditions

- Thank you for your valuable feedback. We fully agree that the original manuscript made overly specific mechanistic interpretations that were not directly supported by the available observations. This concern was also raised by another reviewer, and we have substantially revised the relevant discussions throughout the manuscript.

Specifically, statements directly attributing nighttime nitrate enhancement to NO3/N2O5 chemistry, N2O5 hydrolysis, chloride–nitrate transformation, or specific non-ammonium nitrate formation pathways have been removed or substantially moderated. The revised manuscript focuses on the directly observed temporal behavior and describes enhanced secondary nitrate accumulation under favorable atmospheric conditions without assigning it to a specific unmeasured chemical pathway.

We have also explicitly stated in the limitations that NO3 radicals, N2O5, and ClNO2 were not measured during the campaign and that detailed mechanistic attribution of nighttime nitrate chemistry therefore requires direct measurements of these species in future studies. This revision more clearly separates observational evidence from mechanistic inference.

5. Several figures are information-rich but difficult to read, especially Figures 1, 2, 5, 6, and 7. The authors should improve figure readability by increasing font sizes,

simplifying legends where possible, and ensuring consistent notation for NO_3 particle classes and source factors

- The nomenclature of the four major particle classes has been standardized as NO_3Lv1–NO_3Lv4, and the seven chemically resolved subclasses are now presented consistently throughout the text and figures. Similarly, the complementary NMF solution is consistently presented using the five factors N1–N5.

Figure 1 has been revised to improve the labeling of characteristic ions and particle subclasses, while Figures 2 and 5 have been revised to use clearer terminology for particle number, particulate nitrate mass, and particle size. Figure 6 now consistently displays the five NMF factors and their corresponding interpretations. To reduce the amount of information in the main manuscript, the detailed backward-trajectory figure has been moved to the Supplementary Information, where it is used only to provide transport context for the pollution episodes.

*6. The authors are **strongly recommended** to cite recent work on high-spatiotemporal-resolution monitoring of traffic-related particles in complex urban environments. In particular, Yeganeh, B., Shakerdonyavi, A., Zafarmomen, N., and Taheri, A.: Comprehensive spatiotemporal analysis of long-term mobile monitoring for traffic-related particles in a complex urban environment, Atmospheric Pollution Research, 102870, 2025, is highly relevant. That study provides long-term mobile-monitoring evidence for PM2.5 and black carbon variability and can strengthen the discussion of traffic-related particulate pollution, spatial heterogeneity, combustion-related particles, and urban aerosol source characterization.*

- Thank you for recommending this recent study. We have carefully considered the suggested reference. The work by Yeganeh et al. focuses primarily on high-spatiotemporal-resolution mobile monitoring of traffic-related PM2.5 and black carbon in a complex urban environment, with particular emphasis on spatial heterogeneity and traffic-related particulate pollution. In contrast, the present study focuses on the particle-resolved chemical characteristics, mixing states, semi-quantitative particulate nitrate mass, and complementary source/process analysis of nitrate-containing particles using SPAMS at a regional suburban site.

Although the suggested study is valuable for understanding traffic-related particulate variability, its main research scope and measurement approach differ substantially from those of the present work, and it does not directly address nitrate-containing particle chemistry, SPAMS-based mixing-state analysis, or the mass-constrained semi-quantitative framework developed here. For this reason, we have not added the reference in the revised manuscript, while we appreciate the reviewer for bringing this recent work to our attention.

7. The source interpretations from NMF would benefit from additional uncertainty analysis. Since NMF solutions are not unique, the authors should report how factor number selection was justified and whether sensitivity tests were performed using different factor numbers or initialization settings.

- Thank you for this important suggestion. We agree that uncertainty associated with NMF factor selection should be explicitly evaluated because NMF solutions are not unique. We have therefore strengthened the description of factor-number selection and sensitivity analysis in the revised manuscript and Supplementary Information.

Candidate factor numbers from 2 to 10 were evaluated using multiple rank-survey diagnostics, including the cophenetic correlation coefficient, dispersion, explained variance, residuals, residual sum of squares (RSS), silhouette indices, sparseness, factor stability, and consensus-matrix structure. The four-, five-, and six-factor solutions were examined in greater detail to assess the sensitivity of the chemical interpretation to factor number.

The four-factor solution provided a relatively parsimonious representation but combined several chemically distinguishable patterns, indicating some degree of under-resolution. The six-factor solution showed improved values for several stability metrics and a clearer consensus structure; however, examination of its factor profiles and temporal characteristics indicated that the additional factor mainly represented further subdivision of an already resolved chemical pattern rather than a clearly independent nitrate-related source or atmospheric process. The five-factor solution was therefore selected as the most appropriate compromise among reconstruction performance, stability, parsimony, and chemical interpretability.

For each candidate solution, NMF was performed using the Brunet algorithm with 200 runs, providing repeated initializations for assessment of solution stability. Detailed rank-survey diagnostics, consensus matrices, and the comparison among alternative factor solutions are now provided in the Supplementary Information. We have also emphasized that NMF is used as a complementary source/process analysis and that the factors should not be regarded as unique or definitive source identities.

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