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 "

Comments from the reviewers:

Reviewer#3

This manuscript presents a semi-quantitative framework that integrates single-particle aerosol mass spectrometry (SPAMS), bulk aerosol measurements, and non-negative matrix factorization (NMF) to investigate the composition, mixing state, size distribution, and source contributions of nitrate-containing particles during the autumn–winter period at a regional site in the Yangtze River Delta. The study addresses an important scientific issue, namely the increasing dominance of particulate nitrate in $PM_{2.5}$ *across eastern China and the difficulty of quantitatively interpreting SPAMS observations. The proposed SPAMS–NMF framework represents an interesting attempt to bridge particle-number-resolved measurements and mass-based source apportionment.*

Overall, the manuscript is well organized, the observational dataset is comprehensive, and the scientific questions addressed are timely and relevant. Compared with conventional SPAMS studies, the integration of the semi-quantitative mass-constrained approach with NMF analysis enhances the interpretation of nitrate-containing particles. The following concerns are intended to improve the clarity and robustness of the presentation.

- Thank the reviewer for the positive and constructive evaluation of our manuscript. We clarified the distinction between particle number and estimated particulate nitrate mass and added discussion explaining why different particle populations may contribute disproportionately to these two metrics because of differences in particle size

and nitrate loading. We further expanded the discussion of the broader applicability and limitations of the mass-constrained semi-quantitative framework, emphasizing that the overall strategy is transferable, whereas the regression relationships themselves are likely to require site- and period-specific calibration or validation when applied to other environments. The uncertainty discussion has also been strengthened to clarify that the unexplained variance of the regression model mainly affects the absolute magnitude of the estimated nitrate mass, while relative differences among particle populations and their temporal evolution provide a more robust basis for interpretation. To improve the reproducibility of the particle classification, we added explicit criteria for the manual consolidation following ART-2a clustering, including mass-spectral similarity, diagnostic marker ions, temporal behavior, and size distributions. We also substantially moderated several atmospheric interpretations that were not directly supported by the available measurements. Specifically, mechanistic statements concerning nighttime N_2O_5 chemistry, chloride–nitrate transformation, and non-ammonium nitrate formation were removed or rewritten more cautiously because NO_3 radicals, N_2O_5, and $ClNO_2$ were not directly measured. Similarly, the HYSPLIT analysis is now used only to describe air-mass transport pathways and potential regional influences, rather than to identify specific emission sources. Finally, the manuscript has been carefully proofread to correct grammatical errors, typographical issues, inconsistent spacing, and subject–verb agreement. Overall, these revisions were made to ensure that the conclusions are more closely aligned with the observational evidence and that the scope and limitations of the proposed framework are stated more clearly.All changes have been marked in the revised manuscript.

1. Throughout the manuscript, both particle number and estimated mass concentrations are discussed. However, the implications of the differences between these two metrics are not always sufficiently explained. A brief discussion clarifying why some particle classes contribute disproportionately to number versus mass would improve the interpretation of Figures 2 and 3.

- Thank you for this important comment. We agree that the distinction between particle number contribution and estimated nitrate mass contribution provides

important information on the mixing state and nitrate-loading characteristics of different particle populations.

In the revised manuscript, we have added a discussion clarifying that particle number and particulate nitrate mass represent different aspects of nitrate-containing particle populations. The number contribution reflects the relative abundance of each particle class, whereas the nitrate mass contribution additionally depends on particle size and the amount of nitrate associated with individual particles. Therefore, particle classes with relatively low number fractions can still contribute substantially to nitrate mass if they contain larger particles or higher nitrate loading per particle. Conversely, abundant particle populations may contribute less to nitrate mass when their individual nitrate content is relatively low.

We have added this clarification in the Section 3.1 (line 255-263 in the marked revised manuscript) to improve the interpretation of the differences between number- and mass-based contributions as follows.

"The differences between particle number contribution and estimated nitrate mass contribution offer further insights into the nitrate-loading characteristics of various particle populations. Particle number indicates the frequency of occurrence for each nitrate-containing particle class, whereas nitrate mass contribution is influenced not only by particle abundance but also by particle size and the nitrate content per particle. Consequently, a particle class with a relatively low number fraction may significantly contribute to nitrate mass if it comprises larger particles or exhibits higher nitrate loading. In contrast, a numerically dominant class may contribute less to nitrate mass if the nitrate content per particle is relatively low. Therefore, the discrepancy between number- and mass-based contributions should be interpreted as differences in particle mixing state and nitrate loading, rather than as an inconsistency between the two metrics."

2. The manuscript appropriately emphasizes that the proposed method provides semi-quantitative rather than absolute quantitative estimates. Nevertheless, it would be helpful to further discuss the potential applicability of this framework beyond the

present study. For example, can the regression model be transferred to other observation sites or seasons, or would site-specific calibration always be required? A brief discussion of the general applicability and limitations would increase the broader value of the methodology.

- Thank you for this valuable suggestion. We agree that discussing the broader applicability and limitations of the mass-constrained semi-quantitative framework is important. We have added a discussion in the revised manuscript regarding the transferability of the regression-based approach.

The proposed framework is designed to provide a general strategy for linking particle-resolved SPAMS measurements with bulk nitrate mass constraints, rather than providing a universal calibration equation applicable to all environments. The framework itself, including the integration of particle-resolved nitrate-related signals with independent bulk nitrate measurements, can be transferred to other observation sites and seasons. However, the specific regression coefficients are expected to depend on site- and period-specific aerosol characteristics, including particle composition, nitrate mixing state, size distribution, and atmospheric processing conditions.

Therefore, application to other regions or seasons would likely require site-specific recalibration or validation using concurrent reference measurements (e.g., bulk nitrate observations). Nevertheless, once an appropriate calibration dataset is established, the framework could provide a practical approach for extending SPAMS observations from qualitative particle characterization toward semi-quantitative assessment of particulate nitrate contributions across different environments.

We have added this discussion (line 475-485 in the marked revised manuscript) to clarify both the potential applicability and limitations of the proposed methodology.

"The mass-constrained framework offers a way to extend SPAMS measurements for semi-quantitative analysis of particulate nitrate in various environments. However, several uncertainties and limitations remain when applying this framework beyond the present study. SPAMS detection and ionization efficiencies depend on particle size and composition, and the derived particulate nitrate masses should therefore be interpreted as semi-quantitative. The remaining unexplained variance of the regression model also

introduces uncertainty into the absolute nitrate mass estimates. Therefore, the mass contributions of individual particle subclasses should be interpreted as semi-quantitative estimates, whereas the relative differences among particle populations and their temporal evolution provide a more robust basis for comparison. The regression relationships established here may also vary with aerosol composition, mixing state, season, and measurement environment, indicating the need for site- and period-specific calibration when applying the framework elsewhere."

3. The uncertainty section has been considerably improved. Nevertheless, since the regression model forms the basis of the subsequent analyses, the authors may briefly comment on how the remaining unexplained variance (R = 0.68) could influence the estimated contributions of different nitrate particle classes. Even a qualitative discussion would help readers better understand the robustness of the derived source apportionment.

- Thank you for this important comment. We agree that the remaining unexplained variance of the regression model should be considered when interpreting the estimated nitrate contributions. We have added a clarification in the uncertainty discussion regarding how the regression uncertainty may influence subsequent mass allocation and source/process interpretation.

Specifically, the regression uncertainty mainly affects the absolute magnitude of the estimated particulate nitrate mass associated with individual particle classes. Therefore, the derived nitrate mass contributions should be interpreted as semi-quantitative estimates rather than exact mass values. However, because the same mass-constrained framework and allocation procedure were applied consistently across all particle classes, the relative differences among particle populations and their temporal variations are expected to be more robust than the absolute values. The main conclusions regarding differences in nitrate association among particle populations, size-dependent mixing characteristics, and temporal source/process patterns are therefore interpreted based on relative contributions and combined evidence from SPAMS chemical signatures, independent bulk measurements, and temporal behavior.

This clarification has been added in the revised manuscript (line 478-481 in the marked revised manuscript) as follws.

"The remaining unexplained variance of the regression model also introduces uncertainty into the absolute nitrate mass estimates. Therefore, the mass contributions of individual particle subclasses should be interpreted as semi-quantitative estimates, whereas the relative differences among particle populations and their temporal evolution provide a more robust basis for comparison."

4. The workflow of ART-2a clustering followed by manual consolidation is generally clear. However, it would be beneficial to briefly explain the criteria used during the manual merging process, e.g., spectral similarity, temporal evolution, characteristic marker ions, which would improve the reproducibility of the classification procedure.

- Thank you for this helpful suggestion. We agree that the criteria used for manual consolidation should be clarified to improve the reproducibility of the particle classification procedure. In the revised manuscript, we have added a brief description of the criteria used for merging ART-2a-derived clusters.

Specifically, the manual consolidation was performed based on three complementary criteria: (1) similarity of mass spectral patterns, including the presence and relative intensity of major marker ions; (2) the presence or absence of unique chemical tracers that could justify maintaining separate subclasses; and (3) consistency in temporal behavior and size distributions. ART-2a clusters showing highly similar mass spectra and differing mainly in the relative intensity of several common ions were considered candidates for merging. In contrast, clusters characterized by distinct diagnostic ions (e.g., NH_4^+, K^+, Na^+, or Fe-related signals) or clearly different chemical characteristics were retained as separate subclasses.

These criteria were applied to reduce over-resolution of spectrally overlapping particle groups while preserving chemically meaningful particle populations. The classification was therefore based not only on the ART-2a clustering results but also on chemical interpretation of the averaged mass spectra and particle characteristics.

“After ART-2a clustering, manual consolidation was done to create chemically meaningful particle subclasses. The merging process considered: (1) similarity in averaged ion mass spectra, focusing on marker ions; (2) presence of unique diagnostic ions indicating distinct chemical identities; and (3) consistency in temporal variation and size distribution. Clusters with similar spectral patterns but differing in ion intensities were merged, while those with distinct marker ions or chemical traits were kept separate. This aimed to reduce over-resolution by ART-2a while maintaining meaningful chemical differences among nitrate-containing particles.”

5. The observational support for the inferred nighttime chemical formation mechanism is relatively insufficient. In Section 3.4 and in the Abstract, the authors repeatedly mention that nitrate accumulation during severe pollution episodes, such as PE2 and PE4, was mainly driven by nighttime heterogeneous chemistry, for example N2O5 hydrolysis. However, as the authors acknowledge in the "Limitations" section, this study did not directly measure N2O5, NO3 radicals, or ClNO2. Nevertheless, relatively strong statements are made in the Discussion and Conclusions regarding nighttime N2O5 chemistry, chloride–nitrate transformation, and the formation mechanism of non-ammonium nitrate. The authors are advised to revise these statements using more cautious wording, such as "likely," "suggesting," or "consistent with." To make this key inference more convincing, the authors are also encouraged to conduct semi-quantitative supplementary analyses using the available online observations. For example, the product of NO2 and O3 could be used as an approximate proxy for the nighttime N2O5 production rate, P(N2O5), and its temporal evolution could be analyzed together with relative humidity (RH). Inferring the N2O5 pathway solely from nighttime concentration increases and high-humidity conditions leaves the evidence chain relatively weak.

- Thank you for this valuable comment. We agree that the original manuscript over-interpreted the nighttime nitrate formation mechanism by directly linking enhanced nitrate accumulation during pollution episodes to specific pathways such as N_2O_5 hydrolysis and chloride–nitrate transformation, which cannot be directly verified because NO_3 radicals, N_2O_5, and $ClNO_2$ were not measured during this campaign.

Following this suggestion, we have revised the relevant discussions throughout the manuscript and removed the specific mechanistic interpretations that were not directly supported by observations. In particular, statements regarding nighttime N_2O_5 chemistry, chloride–nitrate transformation, and the formation mechanism of non-ammonium nitrate have been deleted or replaced with more cautious descriptions.

The revised manuscript now interprets the observed nighttime nitrate enhancement as evidence of enhanced secondary nitrate accumulation under conditions favorable for multiphase processing and gas–particle partitioning, without assigning it to a specific chemical pathway. We have also added this limitation to the revised uncertainty discussion, emphasizing that direct measurements of nocturnal oxidants and reactive nitrogen intermediates are required for a more detailed mechanistic attribution.

6. The trajectory analysis occasionally attributes specific source regions solely based on HYSPLIT trajectories. Since trajectories indicate transport pathways rather than emission sources, the wording should be moderated.

- Thank you for this valuable comment. We agree that HYSPLIT backward trajectories represent air mass transport pathways rather than direct evidence of emission sources. We have revised the trajectory-related descriptions throughout the manuscript to avoid overinterpretation. Specifically, source-oriented wording has been replaced by more cautious descriptions of transport pathways and potential regional influences. The revised manuscript now uses trajectory analysis only as supporting information to provide transport context for the observed nitrate-containing particle characteristics and NMF-derived factors, rather than as a standalone method for source attribution.

"Several pollution episodes (PEs) were identified during the campaign, as indicated by the shaded intervals. During PE1 (2–5 November 2024), N5 was the dominant factor, contributing approximately 60% of the total NMF signal during the episode, followed by N3 (~23%). In contrast, N1 and N4 showed relatively weak contributions. The predominance of the mixed secondary nitrate factor suggests that nitrate accumulation during PE1 occurred across chemically diverse particle

populations, while the concurrent contribution from the Na/Cl-associated factor indicates the presence of additional Na/Cl-containing aerosol components. ***Figure S20*** *shows five major air mass trajectory clusters associated with PE1. The dominant cluster (red, 27.08%) represented air masses passing over northern China and the Bohai and Yellow Sea regions, suggesting potential influence from regional transport pathways. The blue and cyan clusters (8.33% and 4.17%) were associated with trajectories passing over the Yellow Sea region, whereas the green cluster (10.42%) represented relatively short transport pathways within nearby inland regions, including Jiangsu and Anhui. The minor pink cluster (2.08%) corresponded to local circulation patterns. Overall, the trajectory analysis suggests that PE1 was influenced by a combination of regional transport and local atmospheric processes.*

During the second observation period (PE2, 20–22 November), both N5 and N1 emerged as significant contributors, accounting for approximately 40% and 30% of the total NMF contribution, respectively. In comparison to PE1, the increased contribution of N1 suggests an enhanced role of ammonium-associated nitrate, while the contribution of N5 indicates ongoing nitrate accumulation within various chemically mixed particle populations. The dominant trajectory clusters (green and yellow) represented air masses passing over northern Jiangsu and Shandong regions, consistent with cold-season northerly transport patterns. These transport conditions may have contributed to the observed enhancement of nitrate-containing particles during this episode.

During PE3 (29 November–4 December), N3 became the largest contributor (~31%), while N4 increased to approximately 15%, substantially higher than during the other episodes. N2 also showed an enhanced contribution compared with its campaign-average level. This combination indicates stronger influences from Na/Cl-associated aerosol, mineral-related particles, and metal-containing aerosol during PE3. Most trajectories remained within the Yangtze River Delta region, suggesting stronger influences from local and regional transport compared with long-range transport. The major trajectory clusters were associated with air masses passing over nearby regions, including Jiangsu, Anhui, and Zhejiang, indicating the importance of regional

circulation under stagnant meteorological conditions. A small fraction of trajectories passed through northwestern inland regions, suggesting that episodic regional transport also contributed during this period.

During the period designated as PE4 (23–27 December), the factors N1 and N5 were predominant, accounting for approximately 35% and 33% of the contributions, respectively, while N4 remained relatively minor. The concurrent significance of the ammonium-associated nitrate and mixed secondary nitrate factors suggests that the accumulation of secondary nitrate was a major characteristic of this episode. Additionally, the presence of a metal-rich factor implies the coexistence of other metal-containing aerosol influences. In summary, PE4 is indicative of the combined effects of secondary nitrate formation and chemically heterogeneous pre-existing particles, rather than the predominance of a single nitrate-containing particle population."

7. The manuscript still contains a number of grammatical and typos, e.g., "wasfollowed", "particlesstarted", "isare", inconsistent spacing, missing articles, and subject–verb agreement. Careful language editing is recommended.

- Thank you for the reviewer for this helpful suggestion. We have checked the entire manuscript and corrected all minor errors.