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#1

This study presents a semi-quantitative framework integrating SPAMS observations, chemical measurements, and NMF source apportionment to investigate nitrate-containing particles in Shanghai. The approach helps bridge the gap between particle-number-based single-particle measurements and mass-based source apportionment, which represents a useful methodological advancement. The manuscript is generally well organized, and the dataset collected at the Dianshan Lake supersite is valuable. The results provide new insights into the mixing state, size distribution, and source contributions of nitrate-containing particles during winter haze episodes. However, several methodological descriptions and interpretations could be clarified. Additional explanations regarding the semi-quantitative calibration framework, the classification of nitrate particle types, and the interpretation of NMF factors would improve the transparency and reproducibility of the study. Some sections of the Results and Discussion could also be streamlined to better distinguish observations from interpretations.

- Thank the reviewer for the positive and constructive evaluation of our manuscript. We appreciate the reviewer's recognition of the value of the Dianshan Lake dataset and the methodological significance of integrating SPAMS observations with chemical measurements and NMF source apportionment. We have clarified the semi-quantitative calibration framework, strengthened the description of NO_3Lv1-NO_3Lv4, improved the interpretation of NO_3Lv4 and EC-containing nitrate particles, linked the mechanistic

conclusions more explicitly to the Results section, and carefully checked the nomenclature and English language throughout the previous revised manuscript. Taking into account the comments from other reviewers, we have made additions and revisions to the previous revised manuscript based on those comments. All changes have been marked in the revised manuscript.

1. Section 2.4 presents the multiple linear regression equation used to estimate nitrate mass concentrations from SPAMS observations. It would be helpful if the authors briefly explained how the predictor variables were selected and whether multicollinearity among meteorological parameters and PM2.5-related variables was evaluated. Such clarification would increase confidence in the robustness of the regression model.

- Thank you for the reviewer for this helpful suggestion. We revised Section 2.4 by adding a paragraph immediately after the MLR equation and variable definitions. The added paragraph explains that the predictor variables were selected according to their physical relevance to nitrate loading and SPAMS detection. Specifically, nitrate peak area and nitrate-containing particle number concentration were used to represent SPAMS-derived nitrate signal intensity and detected particle abundance, respectively, while $PM_{2.5}$ mass concentration provided a bulk aerosol loading constraint. Meteorological variables were included because they can influence nitrate gas-particle partitioning, heterogeneous formation, atmospheric dilution, and particle sampling conditions. We also clarified that all retained predictors in the final regression model were statistically significant ($p < 0.001$), and that the model was used as a semi-quantitative mass-constrained correction rather than as a direct mechanistic model in the revised manuscript (line 120-130 in the revised manuscript) as follows.

"These predictors were selected based on their physical relevance to nitrate loading, SPAMS detection response, aerosol abundance, and meteorological influences on nitrate formation and sampling conditions. In the final regression model, all retained predictors were statistically significant ($p < .001$), indicating measurable associations with nitrate mass concentration. The MLR model was employed as a semi-quantitative, mass-constrained method rather than a direct mechanistic model, focusing on

estimating particulate nitrate mass instead of total particle mass. Bulk nitrate mass concentration measured by MARGA served as the external mass constraint. The estimated particulate nitrate mass was apportioned using SPAMS nitrate-related peak-area data and distributed among SPAMS-derived nitrate-containing particle classes and subclasses based on their relative particle-number fractions. Thus, the reported mass quantities pertain specifically to particulate nitrate mass or concentration. Additional details on the allocation procedure, assumptions, and uncertainties are available in ***Supplement S1****."*

2. The manuscript frequently discusses NO3Lv1-NO3Lv4 particle classes; however, the physical meaning of these four levels is not immediately clear to readers. The authors are encouraged to provide a summary in the main text describing the major spectral characteristics and distinguishing features of each class, rather than relying primarily on the Supplement.

- We appreciate your valuable comments. We appreciate the reviewer's suggestion. We agree that the physical meaning of NO_3Lv1-NO_3Lv4 should be made clearer in the main text. In the revised manuscript, we added a summary paragraph in Section 3.1, immediately after the initial description of the four nitrate-containing particle classes and their averaged mass spectra. This added paragraph clarifies that NO_3Lv1-NO_3Lv4 represent a progressive transition in nitrate enrichment and atmospheric processing rather than four completely independent particle species. The related description is shown as follows (line 172-178 in the revised manuscript).

"The nitrate-containing particles were classified into four groups, NO_3Lv1, NO_3Lv2, NO_3Lv3, and NO_3Lv4. Analysis of the average mass spectra reveals two primary chemical relationships among these groups. Specifically, NO_3Lv1 and NO_3Lv2 exhibited relatively stronger sulfate-related signals and weaker nitrate-related signals, whereas NO_3Lv3 and NO_3Lv4 were characterized by enhanced nitrate fragment ions, particularly NO_2^- and NO_3^-, together with comparatively weaker sulfate signals. While NO_3Lv1 and NO_3Lv2, as well as NO_3Lv3 and NO_3Lv4, can be regarded as two pairs with similar chemical characteristics, these four groups constitute nitrate-containing particles that possess related chemical signatures yet display distinct temporal

characteristics, as elaborated in the subsequent discussion"

3. The authors conclude that NO3Lv4 represents a more aged and secondary-processed nitrate particle class. While this interpretation is reasonable, a short discussion linking its dominant nitrate signals, size distribution characteristics, and associated particle types (e.g., K_N, NaK) would further strengthen the conclusion.

- We thank the reviewer for this constructive suggestion. We have added this discussion in Section 3.3, immediately after the paragraph describing the size-resolved distribution of NO_3Lv4. This location was selected because the paragraph already discusses the size-dependent contributions of subclasses in NO_3Lv4. The added text further links the strong nitrate signals, accumulation-mode size distribution, and associated K-rich and Na-rich nitrate-containing particles, thereby providing a clearer basis for interpreting NO_3Lv4 as the most nitrate-enriched and atmospherically processed particle class. The sentence has been modified in the revised manuscript (line 245-354 in the revised manuscript) as follows.

"NO_3Lv4 showed the strongest carbonaceous contribution at small particle sizes, with NO_3_carbonaceous accounting for ~68% at 0.3 μm. Its contribution decreased overall with increasing diameter and was ~30% at 1.0 μm. By contrast, NO_3_Na-rich increased from ~5% at 0.3 μm to ~31% at 1.0 μm. The NO_3_Fe-rich spectral subclass also increased with particle size, from approximately 1% at 0.3 μm to ~12–14% at 0.8–1.0 μm. Because the atmospheric origin of the Fe-rich particles is being independently evaluated, this size dependence is described here without assigning a specific source.

The comprehensive size-resolved analysis revealed a systematic alteration in the mixing composition of nitrate-containing particles, as opposed to the emergence of fundamentally distinct particle-size modes among NO_3Lv1–NO_3Lv4. Nitrate associated with carbonaceous material was predominantly observed in smaller particle sizes, whereas sodium-rich nitrate-containing particles gained relative prominence in larger particle sizes. These observed patterns were interpreted as indicative of size-dependent variations in particle mixing state and atmospheric processing."

4. Several abbreviations and particle-type names are not always presented consistently throughout the manuscript (e.g., NO3_K_N, K_CN, K_NS, seasalt/SeaSalt,

NO3Lv4/NO3Lv4). Please carefully check the nomenclature and formatting to improve readability and avoid confusion.

- Thank you for your valuable feedback. We have carefully checked the manuscript and Supplementary Information and unified the nomenclature and formatting of nitrate-containing particle classes and particle subclasses. In the revised manuscript, NO_3Lv1-NO_3Lv4 are used consistently for the four major nitrate-containing particle classes. Particle-subclasses names are also standardized throughout the text, tables, and figures.

5. The manuscript highlights the importance of EC-containing nitrate particles throughout the observation period. It would be beneficial to briefly discuss whether the observed EC-nitrate association mainly reflects condensation of secondary nitrate onto pre-existing combustion particles or common source influences.

- We appreciate the reviewer's insightful comment. According to the comments from Reviewer 2, after re-examining the averaged spectra, we agree that the EC-specific signature is not sufficiently distinct to justify maintaining separate NO_3_EC, NO_3_OC, and NO_3_OCEC subclasses based on the current presentation. Rather than over-interpreting the carbonaceous spectral features, we have therefore combined these groups into a broader NO_3_carbonaceous subclass.

6. Some mechanistic interpretations regarding NO3/N2O5 chemistry and ammonium nitrate formation are emphasized in the Conclusions section. The authors may consider explicitly linking these conclusions to the corresponding observations presented in the Results section to improve the logical flow of the manuscript.

- Thank you for your insightful suggestion regarding the NO_3/N_2O_5 chemistry and ammonium nitrate formation. In the previous revised manuscript, we added explanatory text in Section 3.4, immediately after the discussion of the enhanced N3 and N6 secondary inorganic aerosol factors during pollution episodes. This time, we took the comments from Reviewer 2 into account and revised the manuscript accordingly. We deleted the relevant statement in the Conclusions to avoid overstating the role of NO_3/N_2O_5 chemistry, because NO_3 and N_2O_5 were not directly measured in this study. The revised conclusion now states that the possible contribution of nocturnal NO_3/N_2O_5 chemistry should be interpreted as an inferred pathway and requires further verification

by direct measurements in future studies. The revised sentence in the Conclusions is as follows:

"In addition, the absence of direct measurements of NO_3, N_2O_5, and $ClNO_2$ limits detailed mechanistic attribution of nighttime nitrate chemistry. Future studies combining particle-resolved mass spectrometry with direct measurements of nocturnal oxidants, aerosol liquid water and acidity, improved species-specific mass calibration, and multi-site observations across the Yangtze River Delta would further constrain how source mixtures, particle mixing state, and chemical processing jointly regulate nitrate formation."

7. The manuscript would benefit from careful English editing. Several minor grammatical and typographical issues were noted. A thorough language check is recommended before publication. For examples include: Section 4, Line 370: "simultanous" should be "simultaneous". Section 4: "advance understanding nitrate aerosol" could be revised to "advance the understanding of nitrate aerosols".

- We thank the reviewer for pointing out these language and typographical issues. We have carefully checked the manuscript and Supplementary Information for grammar, spelling, formatting, and nomenclature consistency.