

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#2

In this study, the authors measured nitrate-containing particles during autumn-winter in eastern China using single-particle aerosol mass spectrometry, i.e., the SPAMS. A multiple linear regression (MLR)-based semiquantitative method was developed to estimate particulate nitrate mass by combining SPAMS data with MARGA nitrate measurements, PM_{2.5} mass concentrations, and meteorological parameters. Developing such a semiquantitative approach is technically challenging and valuable for the SPAMS community. The methodology, assumptions, calibration procedures, and uncertainties are well described in the Supplement. However, the manuscript should clearly distinguish particulate nitrate mass from particle mass throughout the text. The particle classification forms the foundation of the subsequent scientific interpretation. However, the current classification scheme is overly complex, with too many particle classes and subclasses, making the results difficult to follow. I recommend simplifying the classification framework and reducing the number of particle categories where possible to improve clarity and consistency. Some of the main interpretations are also not sufficiently supported by the presented evidence. In particular, the conclusions regarding nitrate internally mixed with combustion and marine particles are not fully convincing based on the current SPAMS data. In addition, considering the location of the measurement site, lake spray should be discussed as a potential source of Na-containing particles. Although NMF was used for source apportionment, its methodology and added value are not clearly demonstrated. The SPAMS particle

classifications and NMF source factors are presented largely in parallel rather than being effectively integrated, resulting in an unnecessarily complex framework with multiple particle "classes," "types," and source "factors." I recommend simplifying the terminology, presenting NMF as a complementary analysis, and moving detailed NMF results to the Supplement while retaining only the key findings in the main manuscript. Overall, this manuscript addresses a topic well within the scope of the journal, and the methodology and results have the potential to make a valuable contribution. However, substantial revisions to the particle classification, source apportionment, and scientific interpretation are required before the manuscript is suitable for publication. I therefore recommend Major Revision.

- We appreciate the constructive and insightful comments from the reviewer. In response to these comments, we have substantially revised the manuscript to improve its clarity, consistency, and scientific interpretation. Throughout the revised manuscript, we have carefully distinguished particulate nitrate mass from total particle mass and clarified the assumptions, methodology, and uncertainties associated with the MLR-based semi-quantitative approach. The description of how particle-resolved SPAMS information was incorporated into the mass-constrained framework has also been expanded in the main text. We have also reconsidered the particle classification framework. The original classification scheme was simplified by consolidating spectrally overlapping particle categories into seven chemically meaningful nitrate-containing particle subclasses. The criteria used for manual consolidation, including mass spectral similarity, diagnostic marker ions, and consistency in temporal behavior and size distributions, have been added to improve reproducibility. The terminology has been revised accordingly, with “subclasses” used consistently to better represent the hierarchical relationship among particle populations.

Following the reviewer’s suggestions, we have further revised the interpretation of nitrate-containing particles and avoided assigning specific sources where the available observations do not provide sufficient evidence. In particular, previous interpretations related to combustion and marine influences have been moderated. Na-containing nitrate particles are now discussed as Na/Cl-associated particle populations,

considering the potential contributions from multiple environments, including lake spray, rather than being attributed exclusively to marine sources. The limitations in distinguishing Na-containing particle origins using SPAMS alone have also been discussed. The role of the NMF analysis has been clarified and repositioned. In the revised manuscript, NMF is presented as a complementary analysis that provides broader temporal source- and process-related context for the particle-resolved SPAMS observations, rather than as an additional particle classification framework. The construction of the NMF input matrix, factor selection, and interpretation criteria have been further described, while detailed NMF results have been moved to the Supplementary Information. The main text now focuses on the key atmospheric implications derived from combining particle-resolved observations with complementary factor analysis.

In addition, we have carefully revised the atmospheric interpretation throughout the manuscript to avoid overinterpretation. Trajectory analysis is now used to describe air mass transport pathways and potential regional influences rather than direct source attribution. Similarly, discussions of nighttime nitrate formation have been revised to avoid assigning specific chemical mechanisms that were not directly measured. Additional uncertainties related to semi-quantitative mass estimation, NMF non-uniqueness, and the lack of direct measurements of reactive nitrogen intermediates have also been further discussed.

We have answered them point to point in the following paragraphs (the texts in black are the comments, followed by our responses in blue and/or red). In addition, all changes made are marked in the revised manuscript.

Major comments

1. Semi-quantification method: Clarification needed. The mass-constrained semi-quantitative method is used to estimate the particulate nitrate mass, rather than the particle mass. Please state this explicitly to avoid confusion between particulate species mass (i.e., the mass of a species such as nitrate associated with an individual particle) and particle mass (i.e., the total mass of an individual particle). I recommend revising

the terminology consistently throughout both the main manuscript and the Supplement to clearly distinguish these fundamentally different quantities. In addition, Section 2.4 would benefit from a brief description of the allocation of nitrate mass to particle classes and subclasses. Although this procedure is explained in the Supplement and also mentioned in section 2.5, it is a key component of the semi-quantification methodology and should be briefly introduced in section 2.4, with the Supplement cited for further details.

- Thank you for the suggestions. We fully agree that the quantity estimated by our mass-constrained framework is the mass of particulate nitrate, rather than the total mass of individual particles. The original terminology did not consistently distinguish these two fundamentally different quantities.

In the revised manuscript and Supplementary Information, we have therefore systematically replaced ambiguous expressions such as “particle mass” or “mass concentration” with “particulate nitrate mass,” “nitrate mass concentration,” or “nitrate mass contribution,” where appropriate.

We have also clarified the allocation procedure in Section 2.4. Briefly, MARGA nitrate mass concentration is used as the external mass constraint. The fitted nitrate mass is first assigned using the SPAMS nitrate-related peak-area information and is subsequently distributed among the SPAMS-derived particle classes and subclasses according to their relative number fractions. We emphasize that the resulting values are semi-quantitative estimates of particulate nitrate mass and should not be interpreted as measurements of the total mass of individual particles. The detailed assumptions and uncertainties associated with this procedure remain described in Supplement S1.

The detail descriptions have been added in the revised manuscript (line 25-155 in the revised manuscript; S1 in the supplementary material) as follows.

“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**.

2.5 Complementary source apportionment using NMF

To supplement the particle-resolved SPAMS observations with additional source information, NMF was employed on the semi-quantified particulate nitrate dataset, utilizing the "NMF" package in R. The nitrate mass concentrations, allocated to the SPAMS-derived nitrate-containing particle categories via the mass-constrained procedure outlined in Section 2.4, were aligned to a uniform temporal resolution and structured into a non-negative input matrix for NMF analysis. To maintain statistical robustness, zero counts were adjusted to 0.1, and negative values post-allocation were omitted. Consequently, the SPAMS data contributed to the NMF analysis through the temporally resolved, semi-quantified particulate nitrate contributions of chemically resolved particle categories, rather than solely through raw ion intensities.

The optimal number of factors was determined using NMF rank-survey diagnostics and hierarchical clustering, considering metrics like cophenetic correlation, dispersion, explained variance, RSS, profile characteristics, sparsity, and factor stability. A seven-factor solution was chosen for the SPAMS-derived particulate nitrate dataset, and a four-factor solution for the bulk PM_{2.5} chemical composition dataset. Adding more factors improved some fit metrics but decreased factor stability and cluster separation. The NMF factors were analysed by examining their chemical profiles, temporal patterns, and correlations with conventional pollutants and PM_{2.5} components. The bulk PM_{2.5}-based NMF solution served as a benchmark to assess the consistency of source interpretation from the SPAMS dataset. Thus, NMF complemented the SPAMS observations as a source analysis tool, not as another classification method. Detailed rank-survey results, factor profiles, temporal variations, and cross-comparisons between the SPAMS-derived and bulk NMF solutions are provided in **Supplement S4**.

S1. Semi-quantitative calculation of nitrate-containing particles from SPAMS data

SPAMS provides real-time information on the size, number, and chemical composition of individual particles, but it does not directly determine the total mass of individual particles or absolute mass concentrations of specific particulate species. In the present study, the mass-constrained semi-quantitative approach was developed specifically to estimate particulate nitrate mass concentration. It does not estimate the total mass of individual particles. Throughout this Supplement, therefore, nitrate mass concentration refers exclusively to the mass of particulate nitrate associated with the SPAMS-derived particle categories.

S1.1 Workflow of nitrate particle screening and classification

*The workflow of the semi-quantitative calculation is shown in **Figure S3**. Full-component single-particle data were first imported into the data-processing platform. Nitrate-containing particles were then screened using characteristic nitrate fragment ions at m/z 46 (NO_2^-) and m/z 62 (NO_3^-). Particles with clear nitrate-related signals were retained for further analysis. After nitrate screening, the selected particles were classified according to their mass-spectral characteristics. Hierarchical clustering based on peak-area information and correlation relationships was combined with ART-2a clustering and manual consolidation to organize nitrate-containing particles into major classes and chemically resolved subclasses. The processed classification results were then exported for subsequent semi-quantitative nitrate-mass calculation.*

S1.2 Mass-constrained calibration using bulk nitrate measurements

Because SPAMS provides particle counts and relative peak areas rather than absolute particulate nitrate mass concentrations, bulk nitrate concentrations measured by MARGA were used as an external mass constraint. Before regression analysis, SPAMS data, MARGA nitrate concentrations, $\text{PM}_{2.5}$ mass concentrations, and meteorological parameters were synchronized to the same time resolution.

A multiple linear regression (MLR) model was used to relate bulk nitrate mass concentration to SPAMS-derived and environmental variables. The fitted equation was:

$$[\text{NO}_3^-] = -406.353 - 6.387 \times 10^{-7} \times A_{\text{NO}_3} + 0.462 \times [\text{PM}_{2.5}] + 7.174 \times 10^{-5} \times N_{\text{PM}_{2.5}} + 0.356 \times T + 0.532 \times TP + 0.254 \times WS + 0.038 \times RH + 0.386 \times P \quad (R =$$

0.68)

where $[NO_3^-]$ is the nitrate mass concentration measured by MARGA, A_{NO_3} is the nitrate-related peak area measured by SPAMS, $[PM_{2.5}]$ is the $PM_{2.5}$ mass concentration, $N_{PM_{2.5}}$ is the SPAMS particle number concentration within the $PM_{2.5}$ size range, T is temperature, TP is total precipitation, WS is wind speed, RH is relative humidity, and P is atmospheric pressure.

These variables were selected because they are physically related to nitrate loading, aerosol abundance, SPAMS detection response, and meteorological influences on nitrate formation and sampling conditions. In the final regression model, all retained predictors were statistically significant ($p < 0.001$). The regression model was used as a semi-quantitative mass-constrained correction rather than as a direct mechanistic model.

S1.3 Allocation of nitrate mass to particle classes and subclasses

After the bulk nitrate mass was constrained by the regression model, nitrate mass was allocated to nitrate-containing particles using SPAMS-derived particle information. First, the fitted nitrate mass was assigned to nitrate-containing particles according to nitrate-related peak-area information. Then, the nitrate mass contribution was distributed among the major nitrate-containing particle classes and subclasses based on their number fractions.

The nitrate-containing particles were grouped into four major classes, NO_3Lv1 – NO_3Lv4 , and 7 chemically distinct subclasses. These subclasses included potassium-rich nitrate-containing particles (NO_3_K -rich), carbonaceous nitrate-containing particles ($NO_3_carbonaceous$), sodium-rich nitrate-containing particles (NO_3_Na -rich), ammonium-rich nitrate-containing particles ($NO_3_Ammonium$), dust-related nitrate-containing particles (NO_3_Dust), Fe-rich nitrate-containing particles (NO_3_Fe -rich), and other nitrate-containing particles (NO_3_Other).

This allocation procedure converted SPAMS particle-count information and relative ion signals into semi-quantitative particulate nitrate mass concentrations for nitrate-containing particle classes and subclasses. These class- and subclass-resolved nitrate mass concentrations were then used for temporal variation analysis, size-

resolved analysis, and NMF source apportionment.

S1.4 Assumptions of the semi-quantitative approach

The semi-quantitative calculation was based on several assumptions. First, the SPAMS-detected particles were assumed to represent the major nitrate-containing particle population during the observation period. Since only particles with both positive and negative ion spectra were included in the analysis, the chemical classification was more reliable, but particles with weak ion signals may have been excluded. Second, nitrate-related peak areas were used as proxies for relative nitrate signal intensity. However, ion peak areas in SPAMS are not strictly proportional to nitrate mass because they may be affected by laser-particle interaction, particle phase state, matrix effects, and coexisting chemical species. Third, bulk nitrate concentrations measured by MARGA were assumed to provide an appropriate external mass constraint for the SPAMS-derived nitrate-containing particle population. The MARGA nitrate concentration was therefore used to constrain the nitrate mass scale of the SPAMS-derived nitrate information. Fourth, after mass constraint, the relative contributions of nitrate-containing particle subclasses were estimated using their number fractions. This assumes that subclass number fractions can reasonably represent the relative distribution of nitrate-containing particles after nitrate-mass constraint. Therefore, the calculated quantities should be interpreted as semi-quantitative estimates of particulate nitrate mass concentration at the particle-class or subclass level. They do not represent either the total mass of individual particles or direct measurements of the absolute nitrate mass of individual particles.

S1.5 Uncertainties associated with the semi-quantitative method

Several sources of uncertainty should be considered when interpreting the semi-quantitative results. First, SPAMS has size- and composition-dependent detection efficiency. Particles with different aerodynamic diameters, shapes, optical properties, and chemical compositions may have different transmission, sizing, and laser desorption/ionization efficiencies. Therefore, the detected particle population may not fully represent the ambient particle population. This uncertainty mainly affects the absolute magnitude of the estimated particulate nitrate mass concentration, while the

relative temporal trends and differences among dominant nitrate-containing particle classes are expected to be more robust. Second, composition-dependent ionization efficiency may introduce uncertainty. Even if different particles contain similar nitrate mass, their nitrate-related ion signals may differ because of matrix effects and the presence of coexisting species, such as sulfate, organics, metals, chloride, ammonium, and carbonaceous material. Therefore, the nitrate peak area should not be regarded as a direct mass signal. In this study, MARGA bulk nitrate was used as an external mass constraint to reduce the uncertainty caused by the nonlinearity between peak area and nitrate mass. Third, uncertainties may arise from the coupling between SPAMS and bulk measurements. MARGA measures bulk water-soluble nitrate mass concentration, whereas SPAMS detects individual particles within a limited aerodynamic size range and with instrument-specific detection efficiency. Differences in sampling inlet, particle size range, time resolution, and detection principle may lead to imperfect correspondence between bulk nitrate and SPAMS-derived nitrate-containing particles. Therefore, the regression-based calibration was treated as an empirical mass-constrained correction rather than a strict physical conversion factor. Fourth, the MLR model itself introduces uncertainty. The model included SPAMS nitrate peak area, $PM_{2.5}$ mass concentration, SPAMS particle number concentration, and meteorological variables. These variables were selected based on their physical relevance, and all retained predictors were statistically significant. However, nitrate formation is affected by nonlinear atmospheric processes, including gas-particle partitioning, heterogeneous reactions, aerosol liquid water content, aerosol acidity, and atmospheric oxidizing capacity. These processes cannot be fully represented by a linear regression model. The correlation coefficient of the fitted model was $R = 0.68$, indicating that the model captured a meaningful fraction of nitrate variability but still left unexplained variance. Fifth, the allocation of nitrate mass among particle subclasses also carries uncertainty. After mass constraint, nitrate mass was distributed among particle subclasses based on peak-area information and number fractions. Low-abundance subclasses may have larger relative uncertainties because small particle numbers are more sensitive to counting statistics and classification errors. Therefore, subclass-level

nitrate mass concentrations, especially for minor particle types, should be interpreted with caution. Sixth, particle classification and manual consolidation may introduce uncertainty. ART-2a clustering depends on selected parameters, such as vigilance factor, learning rate, and iteration number. Although manual consolidation was performed based on mass spectral characteristics, temporal behavior, and known marker ions, some initially resolved subclasses may have overlapping chemical signatures. For example, particles with strong Na^+ and nitrate-related signals but weak chloride-related peaks were conservatively classified as NO_3 -Na-rich rather than fresh sea-salt particles to avoid overinterpretation of source identity. Finally, the NMF source apportionment inherits uncertainties from the semi-quantitative input matrix. The resolved factors depend on the particle-type mass allocation, classification results, and factor interpretation. Therefore, the NMF factors were interpreted jointly using source profiles, temporal variations, diurnal patterns, correlations with external chemical tracers, and backward-trajectory analysis. Stable sources such as dust and industrial emissions are expected to be more robust, whereas dynamic secondary sources and mixed Na-rich nitrate factors may have larger uncertainties.

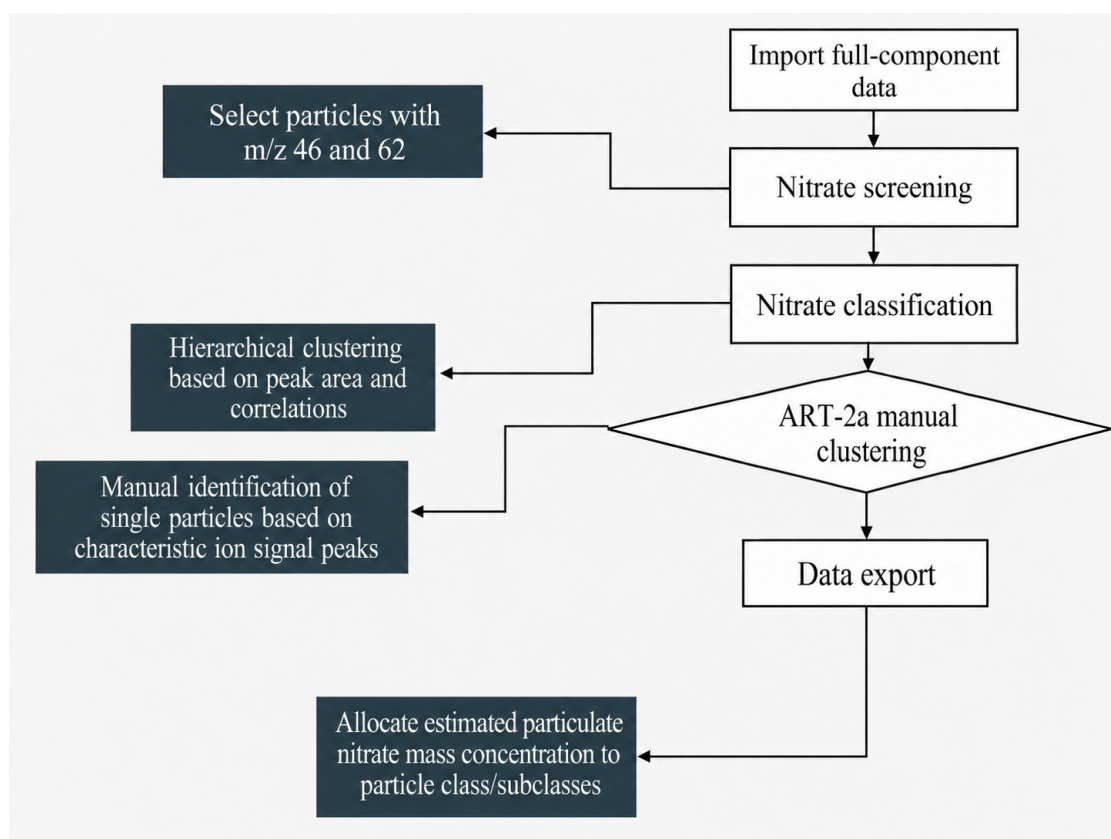


Figure S3. Workflow of the semi-quantitative calculation for nitrate-containing particles based on SPAMS data.

Full-component single-particle data were first imported, and nitrate-containing particles were screened using characteristic nitrate fragment ions at m/z 46 and m/z 62. The selected particles were then classified according to their mass spectral characteristics. Hierarchical clustering was performed based on peak-area information and correlation relationships. ART-2a clustering combined with manual identification based on characteristic ion signal peaks was used to consolidate nitrate-containing particle classes and subclasses. The processed data were exported and used to calculate class- and subclass-resolved particulate nitrate mass concentrations using the semi-quantitative formula. "

2. Section 2.5 (Source Apportionment): Organization and clarity needed. Much of the current content (Lines 117–122 and 124–125) describes the semi-quantification method rather than the source apportionment approach. I suggest moving these paragraphs to Section 2.4, where they fit more naturally. In Section 2.5, please provide a more detailed description of the source apportionment methodology, particularly how SPAMS data were coupled with NMF for source identification. The current description is too brief, making it difficult for readers to understand how the particle-resolved SPAMS measurements were incorporated into the NMF analysis and how the resulting source contributions were determined. I recommend moving some of the key methodological details from the Supplement into the main manuscript so that the source apportionment approach can be understood without requiring readers to consult the Supplement

- Thank you for this helpful suggestion. We agree that the original organization of Sections 2.4 and 2.5 blurred the distinction between nitrate semi-quantification and subsequent source apportionment.

Following the reviewer's recommendation, all procedures related to nitrate mass estimation and allocation have been moved to Section 2.4. Section 2.5 has been rewritten to focus exclusively on the complementary NMF analysis.

We have expanded the methodological description in Section 2.5 to clarify how the particle-resolved SPAMS information was incorporated into the NMF analysis. Briefly, the semi-quantified particulate nitrate contributions associated with the revised SPAMS particle categories were synchronized to a common temporal resolution and organized into a non-negative input matrix for NMF analysis. An independent NMF analysis was also performed using the bulk PM_{2.5} chemical-composition dataset to provide complementary source information and to evaluate the consistency of the particle-resolved source interpretation. The number of factors was selected based on NMF rank-survey diagnostics and solution stability, while factor interpretation was based jointly on factor chemical profiles, temporal and diurnal variations, and associations with independent bulk chemical tracers and conventional air pollutants. Importantly, NMF is no longer presented as an additional particle-classification scheme. Instead, it is used as a complementary source-oriented analysis to provide source context for the particle-resolved SPAMS observations. Key methodological information previously provided only in the Supplementary Information has now been incorporated into the main text, while detailed rank-survey results and factor profiles remain in the Supplement. To make this distinction clearer, we added the following description in the revised manuscript (line 140-156 in the marked revised manuscript; S4 in the supplementary material) as follows.

“2.5 Complementary source apportionment using NMF

To supplement the particle-resolved SPAMS observations with additional source information, NMF was employed on the semi-quantified particulate nitrate dataset, utilizing the "NMF" package in R. The nitrate mass concentrations, allocated to the SPAMS-derived nitrate-containing particle categories via the mass-constrained procedure outlined in Section 2.4, were aligned to a uniform temporal resolution and structured into a non-negative input matrix for NMF analysis. To maintain statistical robustness, zero counts were adjusted to 0.1, and negative values post-allocation were omitted. Consequently, the SPAMS data contributed to the NMF analysis through the temporally resolved, semi-quantified particulate nitrate contributions of chemically resolved particle categories, rather than solely through raw ion intensities.

The optimal number of factors was determined using NMF rank-survey diagnostics and hierarchical clustering, considering metrics like cophenetic correlation, dispersion, explained variance, RSS, profile characteristics, sparsity, and factor stability. A seven-factor solution was chosen for the SPAMS-derived particulate nitrate dataset, and a four-factor solution for the bulk PM_{2.5} chemical composition dataset. Adding more factors improved some fit metrics but decreased factor stability and cluster separation. The NMF factors were analysed by examining their chemical profiles, temporal patterns, and correlations with conventional pollutants and PM_{2.5} components. The bulk PM_{2.5}-based NMF solution served as a benchmark to assess the consistency of source interpretation from the SPAMS dataset. Thus, NMF complemented the SPAMS observations as a source analysis tool, not as another classification method. Detailed rank-survey results, factor profiles, temporal variations, and cross-comparisons between the SPAMS-derived and bulk NMF solutions are provided in **Supplement S4**.

S4 Source apportionment

Both peak areas and particle number exhibited positive correlations with nitrate mass, but the particle number showed a stronger association ($R^2 = 0.4068$) compared to peak areas ($R^2 = 0.1916$), suggesting that particle number provides a more robust proxy for nitrate loading (**Figure S6**). The bulk nitrate mass was initially assigned to individual particles based on peak area and subsequently distributed among subclasses by number fraction. The estimated particulate nitrate mass concentration was apportioned among the 7 subclasses.

Seven chemically resolved nitrate-containing particle subclasses were included in the NMF analysis: NO₃_carbonaceous, NO₃_K-rich, NO₃_Na-rich, NO₃_Ammonium, NO₃_Dust, NO₃_Fe-rich, and NO₃_Other. Their temporally resolved, semi-quantified particulate nitrate contributions were combined with supporting aerosol chemical measurements to construct a non-negative input matrix. NMF (Non-negative Matrix Factorization (NMF) rank evaluation) was used as a complementary source- and process-oriented analysis to identify covarying temporal patterns among the nitrate-containing particle populations and supporting chemical components, rather than as

an additional particle-classification scheme.

*The number of factors were evaluated over candidate ranks from 2 to 10 using the cophenetic correlation coefficient, dispersion, explained variance (evar), residuals, residual sum of squares (RSS), silhouette indices, sparseness, and the structure of the consensus matrices (**Figure S7**). Increasing the factor number generally increased evar and reduced RSS and residuals, as expected with increasing model complexity. Therefore, goodness-of-fit parameters were considered together with factor stability, consensus structure, parsimony, and chemical interpretability rather than being used independently to determine the optimal rank.*

*The four-, five-, and six-factor solutions were examined in greater detail (**Figure S9-S11**). The four-factor solution provided a relatively parsimonious representation but showed greater mixing among several chemically distinct components, indicating some degree of under-resolution. The six-factor solution exhibited higher cophenetic correlation and dispersion and a clearer consensus structure. However, inspection of the factor profiles and temporal behavior indicated that the additional factor mainly represented further subdivision of chemically related components rather than a clearly distinguishable additional source or atmospheric process. Considering model performance, stability, parsimony, and chemical interpretability together, the five-factor solution was selected for subsequent analysis. The five-factor model was obtained using the Brunet algorithm with 200 runs. The comparison with the four- and six-factor solutions supports this compromise between model simplicity and factor resolution.*

*The five factors were interpreted as an ammonium-associated nitrate factor (N1), a metal-rich factor (N2), a Na-/Cl-associated factor (N3), a dust/mineral-related factor (N4), and a mixed secondary nitrate factor (N5) (**Figure S10 and Table S2**).*

The factor profiles and temporal characteristics demonstrate that the NMF factors do not correspond one-to-one with the seven nitrate-containing particle subclasses. The subclasses represent chemically resolved particle populations, whereas the NMF factors represent temporal covariance patterns involving multiple particle subclasses and supporting chemical components. Thus, an individual atmospheric process may

affect several particle subclasses simultaneously, while particles with similar chemical characteristics may occur under different atmospheric source and processing conditions. The full factor profiles, temporal variations, and mean diurnal patterns are shown in **Figure S10**. The five-factor solution exhibits distinct temporal behavior among N1–N5, further supporting their interpretation as different source/process-related patterns.

An independent NMF analysis was also conducted using the ambient PM_{2.5} chemical-composition dataset. Four factors were identified: a dust source (N1), an industrial source (N2), a combustion source (N3), and a composite factor (N4) (**Figure S12 and Table S2**). The bulk PM_{2.5} analysis was based on a different measurement representation and therefore was not expected to produce a factor structure identical to that obtained from the SPAMS-derived particulate nitrate dataset.

Nevertheless, several broad chemical features were consistent between the two analyses. Mineral-related components were represented in both the SPAMS-derived dust/mineral-related factor and the bulk PM_{2.5} dust factor. Metal-rich characteristics were also apparent in both datasets, although the SPAMS-derived factor was interpreted more conservatively because the observed metal composition did not provide sufficient evidence for assignment to a unique industrial source. These similarities provide qualitative support for the presence of mineral- and metal-associated aerosol influences.

Differences were more evident for secondary aerosol. The SPAMS-derived analysis separated an ammonium-associated nitrate factor and a mixed secondary nitrate factor, indicating that secondary nitrate was distributed across multiple chemically distinct particle populations. In contrast, the bulk PM_{2.5} analysis provided a more compositionally aggregated representation of secondary aerosol. The Na/Cl-associated factor identified in the SPAMS-derived analysis also did not show a direct counterpart in the bulk PM_{2.5} solution. These differences are expected because the two datasets emphasize different aspects of aerosol composition: the SPAMS-derived analysis contains information on nitrate mixing state among chemically resolved particle populations, whereas the bulk analysis emphasizes temporal covariance among species

contributing to PM_{2.5} mass.

The bulk PM_{2.5} analysis also identified a distinct combustion factor, whereas the five-factor SPAMS-derived solution did not resolve an isolated combustion-related factor. Instead, carbonaceous- and K-rich nitrate-containing particles contributed to broader nitrate-associated factors, particularly the ammonium-associated and mixed secondary nitrate patterns. This suggests that combustion-derived particle material may undergo substantial secondary nitrate processing after emission, such that its nitrate-containing particle signatures are distributed among multiple atmospheric processing patterns rather than preserved as an isolated source factor.

Overall, the two NMF analyses provide complementary perspectives on aerosol sources and atmospheric processing. The ambient PM_{2.5} NMF emphasizes covariance among mass-dominant chemical components, whereas the SPAMS-derived NMF retains information on the chemical mixing state of nitrate-containing particle populations. Similarities between the two approaches provide supporting evidence for broad mineral-, metal-, and secondary-aerosol influences, while differences reflect the distinct information captured by particle-resolved and bulk-composition measurements.”

3. Four main classes of nitrate-containing particles: Reclassification needed. Please reconsider the particle classification and nomenclature, and revise the corresponding results accordingly. Based on the mass spectra presented in Figure 1a, NO₃Lv1 and NO₃Lv2 exhibit stronger sulfate and weaker nitrate signals than NO₃Lv3 and NO₃Lv4. However, within each pair, the spectra are highly similar. The primary difference between NO₃Lv1 and NO₃Lv2 is that NO₃Lv1 shows somewhat stronger nitrate signals, and a similar relationship is observed between NO₃Lv3 and NO₃Lv4. In fact, the authors also point out the strong links between the pairs NO₃Lv1- NO₃Lv2, NO₃Lv3-NO₃Lv4, based on the cross-correlations shown in the supplement Figure S12. In contrast, the size distributions and diurnal variations suggest that NO₃Lv4 differs substantially from the other particle classes. This apparent inconsistency between the mass spectral similarity and the temporal/size characteristics should be clarified. The size distribution for each class should be shown in the main manuscript or supplement. The current Fig 5 and Fig S15 can not adequately show the actual size distributions of

the four main particle classes, making it difficult to assess whether the proposed classification is supported by particle size characteristics. E.g., for Fig S15, I recommend presenting the particle size distribution of each class as a histogram, normalized either by the total number of particles within that class (sum normalization) or by its maximum bin value. This would allow the intrinsic size-distribution patterns of the individual classes to be compared more directly than the current presentation of particle-class number fraction as a function of particle size. In addition, consider arranging the normalized histograms as vertically stacked panels with a common particle-size axis to facilitate comparison among the different classes. I therefore recommend, at a minimum, combining NO₃Lv1 and NO₃Lv2 into a single category. Similarly, the authors should consider combining NO₃Lv3 and NO₃Lv4, unless there is compelling evidence that they represent distinct particle types. The corresponding figures (Figures 1–5) and related text should then be revised consistently to reflect the updated particle classification.

In addition, the terminology used throughout the manuscript is confusing. The distinction between "nitratecontaining particle classes" and "nitrate-containing particle types" is unclear and should be better defined or simplified to avoid confusion. I suggest using "sub-classes" instead of "types", as this terminology would more clearly reflect the hierarchical relationship between the different particle categories

- We appreciate your important comment. We agree that the averaged mass spectra indicate close chemical relationships between NO₃Lv1 and NO₃Lv2, and between NO₃Lv3 and NO₃Lv4. We therefore carefully re-evaluated whether the original four classes were over-resolved by examining their intrinsic particle-size distributions and temporal behavior in addition to their averaged mass-spectral characteristics.

Following the reviewer's suggestion, we recalculated the intrinsic particle-size distribution of each class by normalizing the particle number in each size bin to the total particle number of the corresponding class. The revised size distributions show that all four classes are dominated by accumulation-mode particles, with a diameter of approximately 0.6 μm . Thus, we agree that particle size alone does not provide sufficient justification for separating the four classes.

However, the four classes exhibit markedly different diurnal behavior even after normalization by their respective mean abundances. In particular, the normalized number-concentration profiles of NO₃Lv1 and NO₃Lv2 show substantially different temporal patterns. NO₃Lv1 reaches its maximum in the early morning (~06:00), whereas NO₃Lv2 peaks in the late afternoon (~16:00). The Pearson correlation between their normalized 24-h mean diurnal profiles is -0.64 . Their estimated nitrate-mass diurnal profiles are also only weakly correlated ($r = 0.29$), with peak times occurring at approximately 12:00 and 15:00, respectively. These differences indicate that the two classes, although chemically related and similar in size distribution, are associated with different temporal behavior and are therefore not simply redundant representations of the same particle population.

A similarly clear distinction is observed between NO₃Lv3 and NO₃Lv4. Their intrinsic particle-size distributions are highly similar, but their diurnal behaviors differ strongly. The normalized number-concentration profiles of NO₃Lv3 and NO₃Lv4 are essentially uncorrelated ($r \approx -0.04$), while their nitrate-mass diurnal profiles are negatively correlated ($r = -0.54$). NO₃Lv4 exhibits a pronounced nighttime enhancement and daytime decrease in nitrate mass, whereas NO₃Lv3 shows a comparatively stronger daytime enhancement.

Based on this reassessment, we have retained the four particle classes. However, we have revised the interpretation of the classification substantially. The four classes are no longer presented as sequential stages of a single nitrate-enrichment or atmospheric-aging pathway. Instead, they are interpreted as chemically related but temporally distinct nitrate-containing particle populations characterized by different combinations of mass-spectral and atmospheric temporal behavior.

To address the reviewer's concern more directly, the revised Supplementary Information now includes class-specific normalized particle-size distributions using a common particle-size axis. We have also added quantitative comparisons of the normalized diurnal profiles and revised the corresponding discussion to acknowledge explicitly that the size distributions of the four classes are broadly similar.

“3.1 Variation of nitrate-containing particle classes

The nitrate-containing particles were classified into four groups, NO₃Lv1, NO₃Lv2, NO₃Lv3, and NO₃Lv4. Analysis of the average mass spectra reveals two primary chemical relationships among these groups. Specifically, NO₃Lv1 and NO₃Lv2 exhibited relatively stronger sulfate-related signals and weaker nitrate-related signals, whereas NO₃Lv3 and NO₃Lv4 were characterized by enhanced nitrate fragment ions, particularly NO₂⁻ and NO₃⁻, together with comparatively weaker sulfate signals. While NO₃Lv1 and NO₃Lv2, as well as NO₃Lv3 and NO₃Lv4, 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.

*The average relative mass spectrum (**Figure 1**) consistently exhibited similar chemical ion signatures. In the positive spectra, NO₃Lv1 and NO₃Lv2 show a strong 39K⁺ presence, accompanied by 23Na⁺ and 37C₃H⁺. The negative spectra displayed a dominant 97HSO₄⁻, while 16O⁻, 35/37Cl⁻, 79PO₃⁻, and 46NO₂⁻/62NO₃⁻ were less prominent, with NO₃Lv2 having higher 46/62 ratios than NO₃Lv1. Similarly, NO₃Lv3 and NO₃Lv4 exhibited strong 39K⁺ in the positive spectra. In the negative spectra, 46NO₂⁻/62NO₃⁻ were more pronounced, and 97HSO₄⁻ was relatively weaker, with NO₃Lv4 showing the strongest 46/62 signatures.*

*Their particle-size distributions were determined by normalizing the particle number within each size bin to the total particle number of the respective class (**Figure S18**). All four groups were dominated by accumulation-mode particles with D_{va} of approximately 0.6 μm, indicating broadly similar size-distribution characteristics.*

*Cross-correlations among nitrate classes revealed stronger links within the NO₃Lv1–NO₃Lv2 and NO₃Lv3–NO₃Lv4. NO₃Lv1 displayed weak correlations with NO₃Lv3–NO₃Lv4 (**Figure S14**). Campaign-scale correlations showed strong covariation within the NO₃Lv1–NO₃Lv2 and NO₃Lv3–NO₃Lv4 pairs. However, campaign-scale covariance does not necessarily imply identical within-day behavior. The former pertains to their co-variation over multi-day pollution timescales, while the latter highlights variations in the recurring diurnal timing of particle abundance.*

The four nitrate-containing particle classes (NO₃Lv1–NO₃Lv4) each exhibited

distinct diurnal patterns in particle number and nitrate mass concentrations (**Figure 2**). For particle number, NO₃Lv1 showed relatively higher abundance during the early morning and reached its maximum at approximately 06:00, whereas NO₃Lv2 increased toward the afternoon and peaked at approximately 16:00. NO₃Lv3 exhibited a pronounced daytime enhancement with a maximum around noon, while NO₃Lv4 showed comparatively elevated nighttime and early-morning abundances and much weaker daytime enhancement. These contrasts remained evident after each 24-h profile was normalized by its respective mean abundance. The normalized number-concentration profiles of NO₃Lv1 and NO₃Lv2 were negatively correlated ($r = -0.64$), whereas those of NO₃Lv3 and NO₃Lv4 were essentially uncorrelated ($r \approx -0.04$). The estimated particulate nitrate mass showed additional differences. NO₃Lv1, NO₃Lv2, and NO₃Lv3 typically displayed maxima during daylight hours, whereas NO₃Lv4 reached its peak during the night and early morning, subsequently declining towards midday. These divergent temporal patterns suggest that the four chemically related particle populations were associated with distinct atmospheric temporal behaviors throughout the campaign (Tao et al., 2023; Tian et al., 2025).”

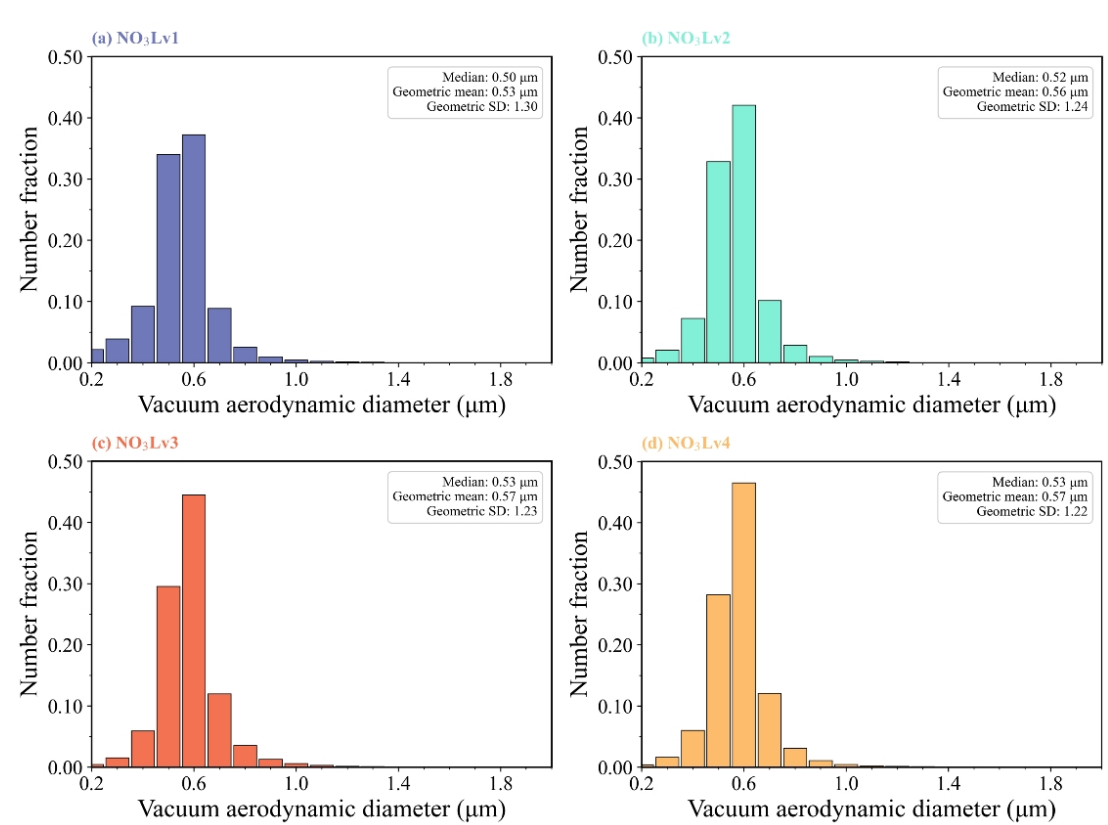


Figure S18. Size-resolved number fraction of nitrate-containing particle classes during the whole observations.

4. Twelf subclasses of nitrate-containing particles (referred to as "types" in the manuscript): The number should be reduced. Similar to the comment #3, please reconsider the classification and evaluate whether particle types with similar spectral markers can be combined. Several categories could appear to differ mainly in the relative intensities of a few ions rather than in the presence of distinct chemical signatures. Consolidating spectrally similar types may simplify the classification, improve its robustness, and make the results easier to interpret.

For example, the following "types" within each group could potentially be merged into a single particle subclass:

- Sub-class 1 (NO3_K-rich): NO3_K_N, NO3_K_S, and NO3_K_CN*
- Sub-class 2 (NO3_OC_EC): NO3_OC, NO3_EC, and NO3_OCEC*

(I cannot identify a clear EC signature in the NO3_EC particle type. Please provide a clearer presentation of the characteristic EC patterns (e.g., the $C_n^{+/-}$), such as a zoomed-in view of the relevant m/z range or annotated mass spectra, to support this classification.

- Sub-class 3 (NO3_Na): NO3_Na-rich and NO3_NaK*

Sub-class 4, 5, and 6 could be dust, Fe, and others. In addition, please carefully re-examine the NO3_Fe particle class. It may or may not be merged into dust class. It may represent an artificial particle type originating from the sampling line or instrument rather than an ambient aerosol type. If the sampling line or inlet components are made of stainless steel, this class would be expected to contain characteristic metal ions, such as m/z 52 (Cr), along with other associated Fe-, Cr-, and Ni-containing ions. Please verify whether this particle class is indeed atmospheric in origin and discuss the possibility of instrumental contamination if appropriate.

Such a simplified classification would make the manuscript easier to follow while preserving the key scientific information

- Thank you for this constructive suggestion. We agree that the previous use of “classes” and “types” obscured the hierarchical relationship among the particle

categories. We have therefore standardized the terminology throughout the manuscript and Supplementary Information. The four NO₃Lv1–NO₃Lv4 groups are referred to as major nitrate-containing particle classes, whereas the chemically resolved groups nested within these classes are now consistently termed subclasses.

We re-evaluated the original 12 subclasses based on their averaged mass-spectral characteristics and agree that several groups were over-resolved. Specifically, the former NO₃_K_N, NO₃_K_S, and NO₃_K_CN groups have been combined into a single NO₃_K-rich subclass; NO₃_OC, NO₃_EC, and NO₃_OCEC have been combined into a broader NO₃_carbonaceous subclass; and NO₃_Na-rich and NO₃_NaK have been combined into a single NO₃_Na-rich subclass.

We retained the ammonium-containing subclass because it is characterized by a distinct NH₄⁺ signal and provides chemically relevant information regarding nitrate neutralization. Dust/mineral particles, Fe-rich particles, and residual particles were also re-evaluated separately.

Consequently, the revised classification contains substantially fewer subclasses and no longer attempts to distinguish particle groups where the available spectra do not provide sufficiently robust diagnostic separation.

After re-examining the averaged spectra, we agree that the EC-specific signature is not sufficiently distinct to justify maintaining separate NO₃_EC, NO₃_OC, and NO₃_OCEC subclasses based on the current presentation. Rather than over-interpreting the carbonaceous spectral features, we have therefore combined these groups into a broader NO₃_carbonaceous subclass. The revised terminology reflects the presence of carbonaceous ion fragments without assigning them uniquely to OC or EC when the diagnostic C_n^{+/-} pattern is not sufficiently clear.

We re-evaluated whether the NO₃_Fe-rich particles should be retained as a separate subclass or merged with the dust-related particles, and we also examined the possibility that the Fe-rich signal originated from stainless-steel components of the inlet or instrument. First, we inspected the average mass spectrum of the NO₃_Fe-rich particles in the metal-ion region. The spectrum is dominated by the Fe-related signal at m/z 56, whereas the signals potentially associated with Cr, Mn, and Ni at m/z 52, 55,

and 58/60, respectively, are comparatively weak. Thus, the NO₃_Fe-rich spectrum does not show a pronounced Fe–Cr–Ni co-signature that would be expected if stainless-steel contamination were the dominant origin. Second, we compared the temporal variation of the SPAMS-derived NO₃_Fe-rich particles with independently measured PM_{2.5} metal concentrations. The NO₃_Fe-rich contribution showed a clear positive relationship with independently measured Fe ($R^2 = 0.3499$) and broadly similar temporal variations, whereas its relationship with Cr was much weaker ($R^2 = 0.0997$). This independent agreement with ambient Fe, together with the weak Cr association, argues against a dominant stainless-steel/instrumental artifact. We also examined whether the NO₃_Fe-rich particles could simply be included within the NO₃_Dust subclass. The temporal behavior of the two subclasses was different, and the relationships of NO₃_Dust with independently measured Ca, Si, and Fe were weak ($R^2 = 0.0018$, 0.002 , and 0.075 , respectively). In contrast, NO₃_Fe-rich showed a substantially stronger relationship with ambient Fe. These results indicate that the Fe-rich and dust-related nitrate-containing particles represent compositionally and temporally distinct particle populations rather than redundant subclasses. Based on this additional evaluation, we have retained NO₃_Fe-rich as a separate chemically defined subclass in the revised seven-subclass classification. However, we have revised the manuscript to avoid assigning it to a unique atmospheric source. The subclass is interpreted only as an Fe-rich spectral population, and the possibility of minor instrumental contributions cannot be completely excluded. The additional spectral and correlation analyses have been added to the Supplementary Information.

Following these revisions, the original 12 chemically resolved groups have been reduced to seven subclasses: NO₃_K-rich, NO₃_carbonaceous, NO₃_Na-rich, NO₃_Ammonium, NO₃_Dust, NO₃_Fe-rich, and NO₃_Other. All the corresponding classification and discussion have been revised accordingly in the revised manuscript and supplementary materials as follows.

“3.2 Chemical characteristics of nitrate-containing particle subclasses

Utilizing a combination of Art-2a and manual consolidation, nitrate-containing particles observed during the autumn-winter period of 2024 were classified into 7

distinct subclasses, including potassium-rich nitrate-containing particles ($\text{NO}_3\text{-K-rich}$), carbonaceous nitrate-containing particles ($\text{NO}_3\text{-carbonaceous}$), sodium-rich nitrate-containing particles ($\text{NO}_3\text{-Na-rich}$), ammonium-rich nitrate-containing particles ($\text{NO}_3\text{-Ammonium}$), dust-related nitrate-containing particles ($\text{NO}_3\text{-Dust}$), Fe-rich nitrate-containing particles ($\text{NO}_3\text{-Fe-rich}$), and other nitrate-containing particles ($\text{NO}_3\text{-Other}$). $\text{NO}_3\text{-Fe-rich}$ subclass was maintained as a distinct spectral category due to its pronounced iron-related signal. When compared with independently measured metal concentrations, this subclass demonstrated a significantly stronger association with ambient iron (Fe) than with chromium (Cr), whereas signals related to Cr, manganese (Mn), and nickel (Ni) in the $\text{NO}_3\text{-Fe-rich}$ mass spectrum were relatively weak (refer to **Supplement S3; Figure S15**). These findings justify the classification of $\text{NO}_3\text{-Fe-rich}$ as a distinct chemically defined population, despite the absence of an identified unique atmospheric source. Given the proximity of the sampling site to Dianshan Lake, locally generated lake-spray aerosols may also contribute to the Na-rich particle population. However, due to the lack of source-specific tracers in the current SPAMS spectra that can distinctly differentiate lake spray from other sodium-containing aerosols, the Na-rich subclass is treated as source-nonspecific in this analysis. Representative relative peak-area mass spectra were generated for the four nitrate classes. During manual consolidation, only particle subclasses representing the top 95% of nitrate-containing particles were retained. The distribution of subclasses across the four nitrate classes is detailed in **Table S1**.

The $\text{NO}_3\text{-K-rich}$ subclass shared strong K^+ signals together with prominent nitrate fragments at m/z 46 (NO_2^-) and 62 (NO_3^-), while the groups were mainly in the relative intensities of sulfate- and carbon/nitrogen-related ions. The $\text{NO}_3\text{-carbonaceous}$ subclass was characterized by prominent carbonaceous fragment ions, including C_3^+ (m/z 36) and C_3H^+ (m/z 37), together with K^+ (m/z 39) in the positive-ion spectrum, while the negative-ion spectrum shows strong nitrate fragments at m/z 46 (NO_2^-) and 62 (NO_3^-) and a weaker sulfate-related signal at m/z 97 (HSO_4^-). The $\text{NO}_3\text{-Na-rich}$ subclass was characterized by prominent Na^+ signals together with nitrate-related ions. The presence or relative intensity of K^+ was not considered sufficient to retain these

groups as separate subclasses. NO_3 _Ammonium was retained as a separate subclass because of its characteristic NH_4^+ signal at m/z 18. NO_3 _Dust and NO_3 _Other were also retained as distinct subclasses (**Figure S15**). NO_3 _Fe-rich was retained as a separate spectral subclass because of its prominent Fe-related signal, although its atmospheric origin and the possibility of inlet- or instrument-related contamination require independent evaluation using associated metal signatures and complementary metal measurements.

Figure 4 illustrates that NO_3 _carbonaceous was the dominant subclass in all four major particle classes, contributing 51.9%, 53.1%, 50.1%, and 55.7% in $\text{NO}_3\text{Lv1}$, $\text{NO}_3\text{Lv2}$, $\text{NO}_3\text{Lv3}$, and $\text{NO}_3\text{Lv4}$, respectively (**Figure 4**). NO_3 _K-rich accounted for 19.7–26.2%, with the highest contribution in $\text{NO}_3\text{Lv2}$, whereas NO_3 _Na-rich contributed 12.9–21.6% and was relatively more abundant in $\text{NO}_3\text{Lv1}$ and $\text{NO}_3\text{Lv3}$. NO_3 _Ammonium contributed 1.5–3.6%, while NO_3 _Dust and NO_3 _Other generally represented minor fractions. The NO_3 _Fe-rich fraction ranged from 2.2% to 7.2% and was highest in $\text{NO}_3\text{Lv4}$.

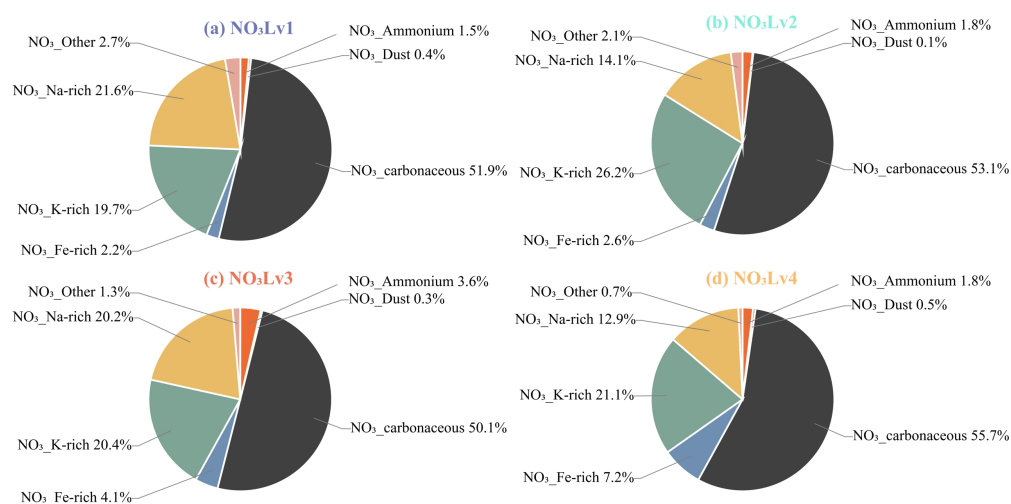


Figure 4: Average contributions of the seven chemically resolved subclasses to the estimated particulate nitrate mass associated with the four major nitrate-containing particle classes: (a) $\text{NO}_3\text{Lv1}$, (b) $\text{NO}_3\text{Lv2}$, (c) $\text{NO}_3\text{Lv3}$, and (d) $\text{NO}_3\text{Lv4}$.

The high fraction of NO_3 _carbonaceous in four classes suggests an accelerated formation and aging of secondary nitrate under high RH and oxidizing conditions

characteristic of the autumn-winter period over the Yangtze River Delta region ([Zang et al., 2022](#)). The temporal evolution of NO_3 _Na-rich and NO_3 _K-rich subclasses showed clear variability among the four major nitrate-containing particle populations (**Figures S16–S17**). NO_3 _Na-rich particles exhibited episodic enhancements during high nitrate-loading periods, with relatively larger contributions in several pollution events in November and December. However, their fractional contribution varied substantially among four classes, indicating that Na-rich particles were not associated with a single temporal pattern but were distributed among chemically distinct nitrate-containing populations. In comparison, NO_3 _K-rich particles showed persistent contributions throughout the campaign, with enhanced abundance during several nitrate pollution periods. These observations suggest that Na- and K-containing particle populations represent important but temporally variable particle matrices for nitrate accumulation, rather than indicating a single dominant source or formation pathway ([Chen et al., 2016](#)).

3.3 Size distributions and size-resolved subclass composition of nitrate-containing particles

The three classes $\text{NO}_3\text{Lv}2$, $\text{NO}_3\text{Lv}3$, and $\text{NO}_3\text{Lv}4$ exhibit highly similar size patterns, all peaking at $D_{\text{p}} 0.5\text{--}0.7\ \mu\text{m}$, suggesting comparable secondary formation and aging processes (**Figure S15**). **Figure 5** further shows the size-resolved composition of the seven revised nitrate-containing particle subclasses. NO_3 _carbonaceous was generally the dominant subclass at smaller and accumulation-mode sizes, whereas the relative contribution of NO_3 _Na-rich tended to increase with particle diameter. NO_3 _K-rich represented another substantial fraction, although its size dependence varied among the four major classes. This finding corroborates previous observations showing that ammonium nitrate typically dominates the accumulation mode in wintertime urban and regionally influenced air ([Cheng et al., 2018](#)).

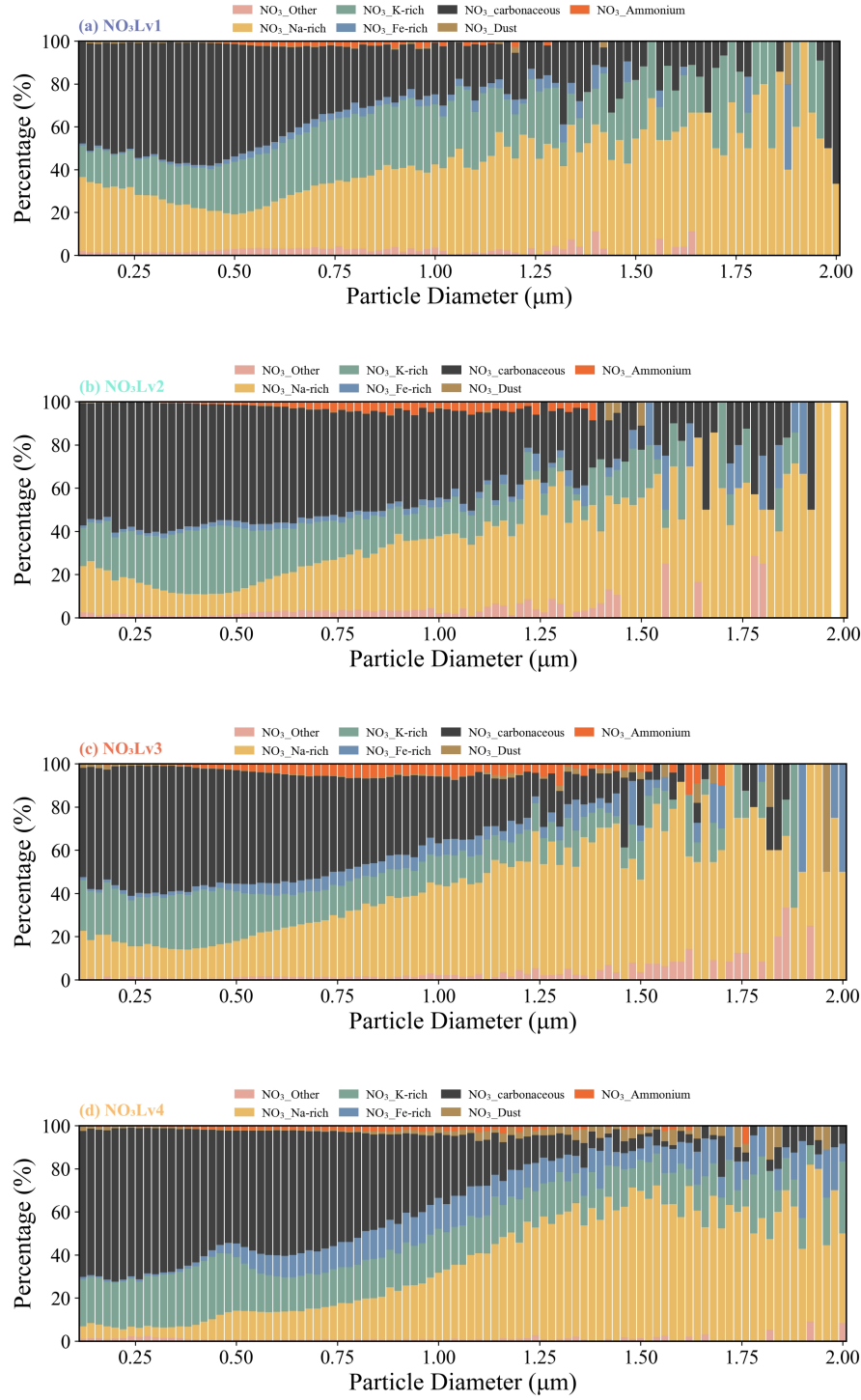


Figure 5: Size-resolved subclass composition of the four nitrate-containing particle classes. Stacked bars show the relative contributions of the seven revised subclasses as a function of vacuum aerodynamic diameter (D_{va}) for (a) NO_3Lv1 , (b) NO_3Lv2 , (c) NO_3Lv3 , and (d) NO_3Lv4 . Each color denotes a specific nitrate-containing particle subclasses, including potassium-rich nitrate-containing particles (NO_3_K -rich), carbonaceous nitrate-containing particles ($NO_3_carbonaceous$), sodium-rich

nitrate-containing particles (NO₃_Na-rich), ammonium-rich nitrate-containing particles (NO₃_Ammonium), dust-related nitrate-containing particles (NO₃_Dust), Fe-rich nitrate-containing particles (NO₃_Fe-rich), and other nitrate-containing particles (NO₃_Other).

For NO₃Lv1, NO₃_carbonaceous accounted for approximately 52% of the particles at Dva 0.3–0.5 μ m and decreased toward larger sizes, whereas the contributions of NO₃_K-rich and NO₃_Na-rich became increasingly important. At approximately 1.0 μ m, NO₃_Na-rich represented ~39% of the subclass composition, compared with ~24% for NO₃_carbonaceous. In NO₃Lv2, NO₃_carbonaceous remained dominant through most of the accumulation mode, decreasing from ~60% at 0.3 μ m to ~41% at 1.0 μ m. In parallel, NO₃_Na-rich increased from ~12% to ~36%, while NO₃_K-rich was relatively abundant around 0.3–0.5 μ m and decreased toward larger particle sizes.

A similar but more pronounced size-dependent shift was observed for NO₃Lv3. The NO₃_carbonaceous fraction decreased from ~59% at 0.3 μ m to ~31% at 1.0 μ m, whereas NO₃_Na-rich increased from ~15% to ~42% and became one of the dominant subclasses near the super micron range. NO₃_Ammonium and NO₃_Fe-rich remained comparatively minor but showed modest increases within the accumulation-mode size range.

NO₃Lv4 showed the strongest carbonaceous contribution at small particle sizes, with NO₃_carbonaceous accounting for ~68% at 0.3 μ m. Its contribution decreased overall with increasing diameter and was ~30% at 1.0 μ m. By contrast, NO₃_Na-rich increased from ~5% at 0.3 μ m to ~31% at 1.0 μ m. The NO₃_Fe-rich spectral subclass also increased with particle size, from approximately 1% at 0.3 μ m to ~12–14% at 0.8–1.0 μ m. 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 NO₃Lv1–NO₃Lv4. 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.

S3 Evaluation of the NO₃_Fe-rich subclass

The NO₃_Fe-rich subclass was further evaluated to determine whether it represented a distinct atmospheric particle population, a dust-related component, or a possible inlet/instrument artifact. The average mass spectrum of NO₃_Fe-rich particles was dominated by the Fe-related ion at m/z 56, whereas Cr-, Mn-, and Ni-related signals at m/z 52, 55, and 58/60, respectively, were comparatively weak. The absence of a pronounced Fe–Cr–Ni co-signature does not support stainless-steel contamination as the dominant origin of this subclass.

To further evaluate its atmospheric relevance, the temporally resolved NO₃_Fe-rich contribution was compared with independently measured PM_{2.5} metal concentrations. NO₃_Fe-rich showed a clear positive relationship with ambient Fe ($R^2 = 0.3499$), and the two-time series exhibited broadly consistent temporal variations. In contrast, the correlation between NO₃_Fe-rich and Cr was much weaker ($R^2 = 0.0997$). These results provide independent support for an ambient Fe-related contribution to the NO₃_Fe-rich particle population, although a minor instrumental contribution cannot be completely excluded.

We additionally examined whether NO₃_Fe-rich should be merged with the NO₃_Dust subclass. The relationships between NO₃_Dust and independently measured Ca, Si, and Fe were weak ($R^2 = 0.0018$, 0.002, and 0.075, respectively), and its temporal behavior differed from that of NO₃_Fe-rich. Thus, the Fe-rich and dust-related subclasses do not appear to represent redundant particle populations. NO₃_Fe-rich was therefore retained as a separate chemically defined subclass in the revised classification. Because the available measurements do not uniquely determine its atmospheric source, no specific industrial, mineral, or other source attribution is assigned to this subclass.

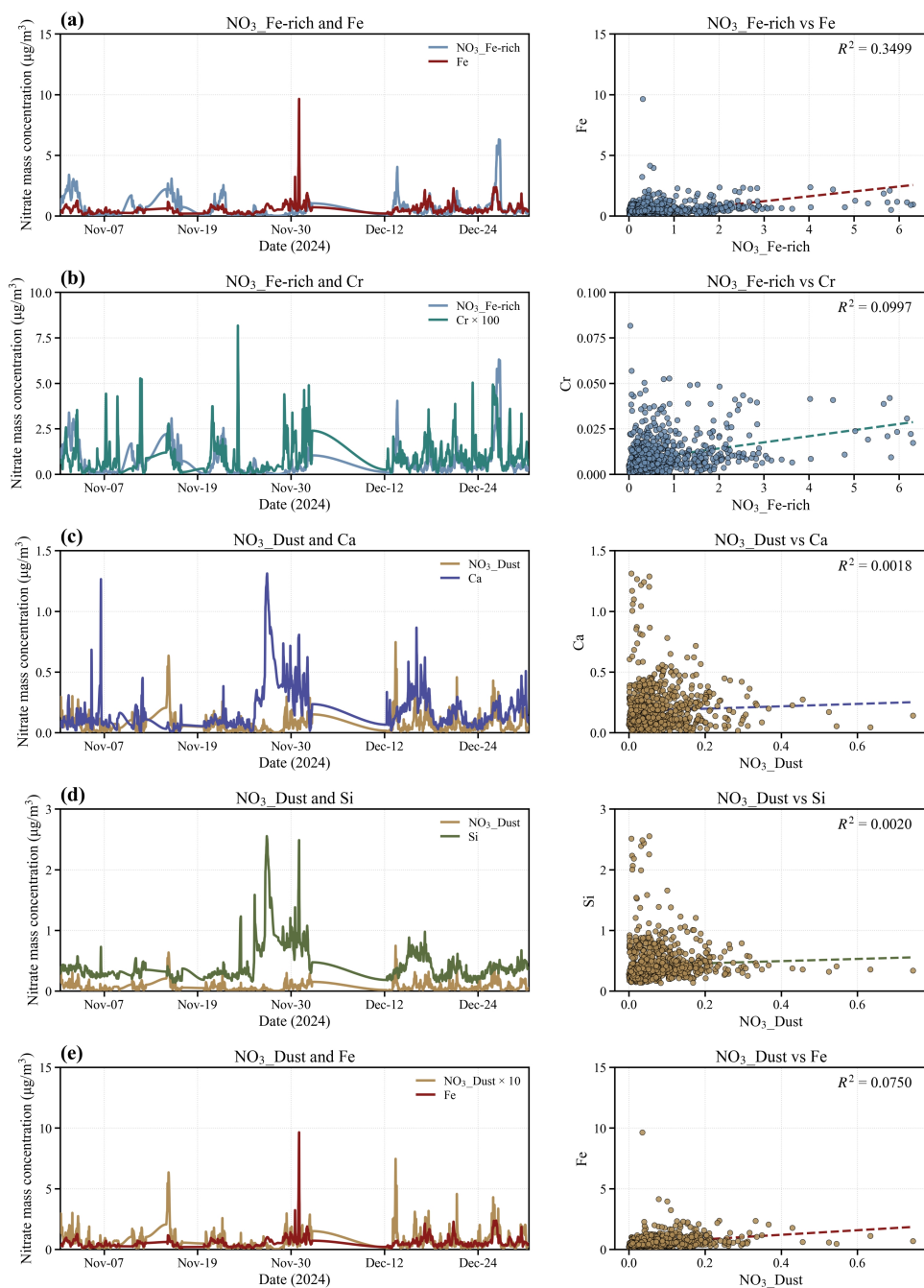


Figure S5. Evaluation of the NO_3 _Fe-rich subclass. (a) Relationship and temporal comparison between the SPAMS-derived NO_3 _Fe-rich contribution and independently measured $\text{PM}_{2.5}$ Fe. (b) Relationship and temporal comparison between NO_3 _Fe-rich and $\text{PM}_{2.5}$ Cr. (c–e) Relationships of the NO_3 _Dust subclass with independently measured Ca, Si, and Fe, respectively.”

5. *Revision of the sea-salt and marine emission interpretations.* The authors suggest that nitrate is internally mixed with species from marine emissions. However, the evidence presented does not sufficiently support this interpretation. For example, the mass spectra shown do not clearly indicate the presence of sea salt particles or other definitive marine tracers. Please note that the presence of Na-containing particles, even those with relatively large particle sizes, does not necessarily indicate a sea-salt source. Such particles could also originate from other sources, including lake spray, mineral dust, road salt, or industrial emissions. Furthermore, there is no clear mass spectral evidence supporting the identification of either fresh or aged sea-salt particles in this study. Consequently, the corresponding interpretations are not justified by the data presented and should be revised or removed. In particular, the interpretation of these particles as chloride-depleted sea salt in the manuscript appears to be based primarily on the presence of Na-containing particles together with nitrate. However, this inference is not uniquely supported by the SPAMS data. Without additional evidence demonstrating that these particles were originally sea salt (for example, characteristic chloride-related ions, other diagnostic sea-salt signatures, or independent supporting measurements) the observed Na-rich nitrate spectra cannot be unambiguously attributed to chloride-depleted sea salt. In addition to the back-trajectory analysis, please provide further evidence to support the proposed marine influence. Otherwise, I recommend removing this interpretation and the corresponding discussion from the manuscript.

- We appreciate your comment. We agree that the main manuscript over-interpreted the origin of the Na-containing nitrate particles.

Our particle-classification procedure itself did not require a sea-salt origin for these particles. Indeed, as clarified in the Supplementary Information, particles characterized by strong Na⁺ and nitrate-related signals but weak chloride signals were conservatively classified as Na-rich nitrate-containing particles rather than fresh sea-salt particles specifically to avoid over-interpreting their source identity.

However, we acknowledge that the subsequent discussion in the main manuscript went beyond what can be uniquely supported by the SPAMS spectra, particularly

through the use of the terms “chloride-depleted sea salt,” “aged sea salt,” and “chloride–nitrate replacement.”

We have therefore removed these interpretations. The revised manuscript refers to these particles only as Na-rich nitrate-containing particles and explicitly recognizes that multiple sources, including local lake spray, mineral-related sources, industrial emissions, and potentially regionally transported marine aerosol, may contribute to this population. Backward trajectories crossing marine regions are now used only to characterize transport pathways and are not treated as proof of a marine origin for individual Na-rich particles.

6. Potential contribution of lake spray particles should be discussed. Considering the location of the measurement site, particles originating from the nearby lake would also be expected to contribute to the observed particle population. However, such a source is not considered or discussed in the manuscript. Please discuss the potential contribution of lake spray particles and explain how they were distinguished from other Na-containing particle types.

- Thank you for raising this important point. We agree that the proximity of the Dianshan Lake site makes local lake-spray particles a plausible contributor to the observed Na-containing particle population and that this possibility should have been considered in the original manuscript.

We have therefore added a discussion of lake spray as one potential source of the Na-rich nitrate-containing particles. Importantly, the available SPAMS spectra do not provide a unique tracer that allows lake-spray particles to be quantitatively distinguished from other Na-containing sources. We therefore do not assign the revised Na-rich subclass to a unique source.

Instead, the revised manuscript explicitly states that the Na-rich nitrate-containing particles may represent a mixture of contributions from local lake spray and other Na-containing sources, with possible regional or marine contributions depending on air-mass history. Additional measurements of lake-water composition or source-specific chemical tracers would be required to distinguish these contributions quantitatively. The explain descriptions have been added in the revised manuscript (Line 276-279) as

follows.

“Given the proximity of the sampling site to Dianshan Lake, locally generated lake-spray aerosols may also contribute to the Na-rich particle population. However, due to the lack of source-specific tracers in the current SPAMS spectra that can distinctly differentiate lake spray from other sodium-containing aerosols, the Na-rich subclass is treated as source-nonspecific in this analysis”.

7. NMF source apportionment should be presented as a complementary analysis. The purpose and added value of the NMF analysis are not sufficiently clear. The manuscript introduces seven NMF factors (N1–N7), in addition to the multiple SPAMS particle classifications, resulting in several parallel classification schemes that make the overall interpretation unnecessarily complex. It is unclear what additional scientific insight the seven NMF factors provide beyond the particle classifications already derived from the SPAMS data. Ideally, the SPAMS measurements should form the scientific foundation, with the NMF analysis serving as a complementary tool that enhances and strengthens the interpretation rather than introducing another layer of classification. The combined use of SPAMS and NMF should generate scientific insights that neither method could provide independently, that is, the whole should be greater than the sum of its parts. The NMF analysis appears to play a supporting role rather than representing the primary scientific focus of the manuscript. I therefore suggest considering moving some of the NMF-related figures to the Supplement and reducing the emphasis on NMF in the main text. Likewise, I recommend reconsidering the use of "SPAMS–NMF" in the title, as it implies that the coupling of the two methods is the central contribution of the study. In its current form, however, the manuscript does not fully demonstrate the added value or scientific novelty of the SPAMS– NMF coupling. Placing greater emphasis on the particle-resolved SPAMS measurements and presenting the NMF analysis as a complementary tool would result in a clearer and more focused manuscript.

- Thank you for this insightful comment. Our original manuscript placed excessive emphasis on NMF and did not sufficiently distinguish its role from that of the particle-resolved SPAMS classification. In the revised manuscript, SPAMS particle-resolved

chemical characterization is now presented as the primary scientific foundation of the study. NMF is used only as a complementary source-oriented analysis to identify covarying chemical components and to provide additional context for interpreting the temporal evolution and pollution episodes.

Following the reviewer's suggestion, we have substantially reduced the presentation of individual NMF factors in the main text. Detailed factor profiles, temporal variations, and diagnostic information have been moved to the Supplementary Information. Only the NMF findings directly relevant to the interpretation of the SPAMS observations and major pollution episodes are retained in the main manuscript.

In addition, because the SPAMS particle classification has been simplified, the NMF analysis has been repeated using the revised particle-category inputs to maintain consistency between the two analyses.

We have also revised the manuscript to avoid referring to the NMF factors as another particle-classification system. Instead, they are referred to as source-related factors or covarying chemical factors.

Finally, we agree that the original title placed excessive emphasis on the SPAMS–NMF coupling. We have therefore removed “SPAMS–NMF framework” from the title.

“New title: Mass-constrained characterization of nitrate-containing particles in eastern China using single-particle aerosol mass spectrometry

3.4 Source and process of nitrate-containing particles during pollution episodes

*To provide source and atmospheric-process context for the particle-resolved SPAMS observations, NMF was applied to time-resolved nitrate contributions from 7 subclasses and other chemical data. This analysis aimed to identify temporal patterns and examine related atmospheric conditions, not to create a new particle classification. A five-factor solution was chosen based on model performance, stability, simplicity, and chemical interpretability. The five factors were interpreted as an ammonium-associated nitrate factor (N1), a metal-rich factor (N2), a Na/Cl⁻ associated factor (N3), a dust/mineral-related factor (N4), and a mixed secondary nitrate factor (N5). Detailed rank-selection diagnostics, factor profiles, time series, and diurnal variations are provided in **Supplement S4**.*

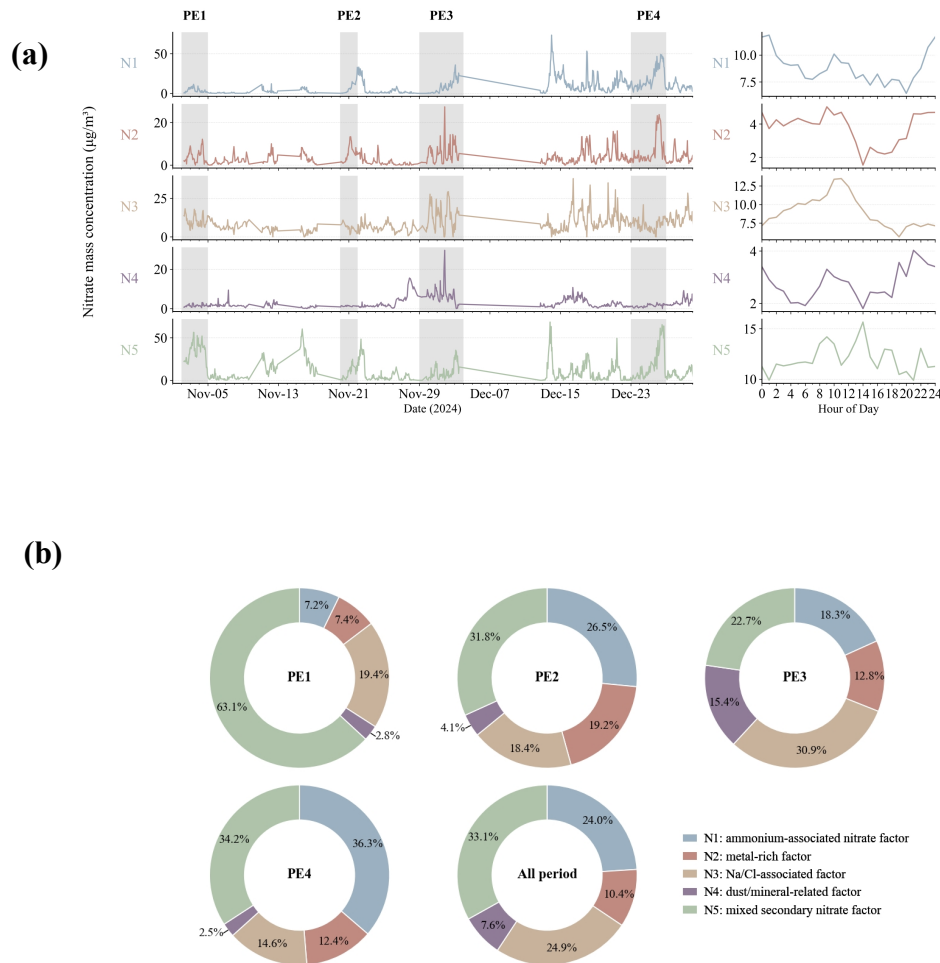


Figure 6: (a) Time series (left) and diurnal profiles (right) of factor-resolved nitrate mass concentration for five nitrate-related source factors (N1–N5) resolved over the full observation period. (b) Source contribution of N1–N5 factors to total particulate nitrate during four pollution episodes and the entire campaign. The factors are interpreted as: N1 – ammonium-associated nitrate factor, N2 – metal-rich factor, N3 – Na/Cl associated factor, N4 – dust/mineral-related factor, N5 – mixed secondary nitrate factor.

The ammonium-associated nitrate factor (N1) exhibited the strongest correlation with the NO_3 _Ammonium subclass and showed covariation with NO_3 _Na-rich, NO_3 _K-rich, NO_3 _carbonaceous, NH_4^+ , and sulfate-related components. This pattern suggests that the formation of ammonium-associated nitrate was not restricted to a single chemically homogeneous particle population; rather, it occurred in conjunction with nitrate on several pre-existing particle types. N1 accounted for 24.0% of the campaign-

average NMF contribution. The diurnal profile was relatively elevated during nighttime and early morning, decreasing toward the afternoon, indicative of the temperature dependent gas–particle partitioning of ammonium nitrate.

The metal-rich factor (N2) exhibited strong correlations with chromium (Cr), nickel (Ni), manganese (Mn), zinc (Zn), iron (Fe), and copper (Cu), together with weaker carbonaceous signatures. This factor contributed 10.4% to the overall factor composition. The observed characteristics suggest intervals of increased metal-laden aerosol presence. While anthropogenic and industrial emissions are potential contributors to this factor, a precise industrial source attribution was not pursued due to the possibility of these metals originating from diverse sources. Consequently, N2 is conservatively interpreted as a metal-rich factor defined by its compositional attributes.

The Na/Cl-associated factor (N3) exhibited the strongest correlation with Na^+ and a significant association with Cl^- , whereas its correlation with the chemically defined NO_3 _Na-rich subclass was considerably weaker. On average, N3 accounted for 24.9% and demonstrated a notable enhancement during the daytime, with its mean diurnal peak occurring in the late morning. The absence of a one-to-one correspondence between N3 and the NO_3 _Na-rich subclass indicates that the variability of Na-rich chemicals within the broader aerosol population is not synonymous with the Na-rich nitrate-containing particles identified by SPAMS. Considering the proximity of Dianshan Lake and the presence of multiple potential sources of Na/Cl-containing aerosols, this factor was interpreted as a Na/Cl-associated factor rather than being attributed to a specific source.

The dust/mineral-related factor (N4) was characterized by the presence of calcium (Ca) and silicon (Si) and was further correlated with barium (Ba) and iron (Fe), thereby indicating a distinct mineral-particle signature. This factor accounted for the smallest average contribution across the campaign, at 7.6%. Notably, it exhibited relatively low concentrations during daytime hours, with a tendency to increase in the evening. This pattern suggests episodic influences from resuspended and/or regionally transported mineral aerosol.

The mixed secondary nitrate factor (N5) accounted for the largest campaign-

average contribution (33.1%). It was strongly associated with several SPAMS-derived nitrate subclasses, particularly NO_3 _carbonaceous, NO_3 _Dust, NO_3 _Fe-rich, and NO_3 _Other, and showed substantial associations with NO_3 _Na-rich and NO_3 _K-rich, together with NH_4^+ and SO_4^{2-} . This factor does not represent a single particle source but rather reflects nitrate accumulation on chemically diverse pre-existing particles. N5 exhibited a clear daytime enhancement, reaching its mean maximum in the early afternoon.

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.”

Minor comments

Page (P)1 Line (L)15: *The term "winter observation" is used in the abstract, while "autumn–winter" is used in several places in the manuscript. Please keep the terminology consistent throughout the manuscript.*

- We have changed “winter observations” to “autumn–winter observations” and used “autumn–winter” consistently throughout the manuscript, corresponding to the observation period from 1 November to 31 December 2024

PIL17: *Is the 0.5-0.7 μm D_p or D_a or D_{va} ? The particle sizes reported by SPAMS are typically vacuum aerodynamic diameters (D_{va}), not physical diameters (D_p). Unless the authors have converted the measurements to physical diameters, please replace D_p with D_{va} (or clearly define the diameter metric used) throughout the manuscript.*

- Thank you for pointing this out. The particle diameter reported by the SPAMS corresponds to the vacuum aerodynamic diameter (D_{va}), derived from particle velocity and calibrated using polystyrene latex standards. No conversion from the measured aerodynamic size to physical diameter was performed in this study.

We have therefore replaced D_p with D_{va} throughout the manuscript and now explicitly define D_{va} as the vacuum aerodynamic diameter measured by SPAMS at its first occurrence. Corresponding figure axes, captions, and Supplementary Information have also been revised for consistency. All particle-size values and size ranges discussed in the manuscript therefore refer to D_{va} unless otherwise stated.

PIL20: *Please remove the term "chloride-depleted sea salt," as no evidence is presented to support this interpretation.*

- The term “chloride-depleted sea salt” has been removed because the available spectra do not uniquely establish a sea-salt origin or chloride depletion. The particles are now described conservatively as Na-rich nitrate-containing particles

PIL24-26: *The results cannot indicate NO_x - NH_3 chemistry, please revise.*

- The original statement was too mechanistic given that the measurements do not

directly resolve the complete NO_x–NH₃ reaction pathway. We have therefore removed the statement concerning “joint NO_x–NH₃ chemistry” from the Abstract. The revised abstract has been modified as follows.

*“**Abstract.** Particulate nitrate constitutes a significant component of winter haze in eastern China. However, its particle-scale heterogeneity and atmospheric context remain inadequately understood. To address this, we conducted an autumn–winter observational campaign at the Dianshan Lake regional site in suburban Shanghai, employing single-particle aerosol mass spectrometry (SPAMS) in conjunction with bulk aerosol measurements. A mass-constrained semi-quantitative framework was utilized to estimate particulate nitrate mass, while non-negative matrix factorization (NMF) provided complementary insights into the underlying processes. Our analysis identified four principal nitrate-containing particle classes (NO₃Lv1–NO₃Lv4), each exhibiting broadly similar accumulation-mode vacuum aerodynamic size distributions with modal diameters near 0.6 μm yet demonstrating distinct diurnal behaviours. This suggests the presence of chemically related but temporally differentiated particle populations. Seven chemical subclasses were resolved, with carbonaceous nitrate-containing particles predominating across all four classes (51.3–55.6%). Na-rich particles gained relative prominence at larger diameters. NMF analysis identified distinct patterns characterized by ammonium-associated nitrate, metal-rich components, Na/Cl-associated elements, dust/mineral-related substances, and mixed secondary nitrate. Notably, the mixed secondary factor accounted for the largest contribution at 33.1%. These findings indicate that nitrate accumulation is a result of complex interactions involving secondary formation processes, particle mixing states, and regional transport mechanisms, rather than being attributable to a singular source pathway.”*

P3L71: *D_p generally refers to the physical particle diameter. If the values reported here correspond to aerodynamic diameter or vacuum aerodynamic diameter, as commonly used in SPAMS, please use the appropriate notation (D_a or D_{va}) throughout the manuscript to avoid confusion.*

- We have revised the particle-diameter notation consistently throughout the

manuscript to Dva.

P3L72: *Add a space between “studies” and “(“. Similar formatting issues are found in several other places throughout the manuscript. Please review the manuscript carefully and correct them consistently.*

- We have also carefully checked the manuscript for similar spacing and formatting issues and corrected them consistently.

P3L79: *It is not clear what is meant by "MASS mode." Readers who are not familiar with the instrument or methodology may not understand this terminology. Please provide a brief explanation (at least in the Supplementary Information) and clarify whether there are other operating modes. Otherwise, I suggest simply removing "(MASS mode)" if it is not essential.*

- We agree that the term “MASS mode” was insufficiently defined and could be confusing. We have removed the ambiguous use of “MASS mode” and now describe the measurement procedure directly. Particles detected by the two sizing lasers are referred to as sizing events, whereas particles that were subsequently ionized by the 266-nm laser and yielded valid mass spectra are referred to as mass-spectral events. Only particles for which valid positive- and negative-ion mass spectra were obtained were included in the chemical classification.

P3L84: *Add “(CO)” after carbon monoxide to keep consistency.*

- “Carbon monoxide” has been changed to “carbon monoxide (CO).”

P4L93: *Change the color of “the” to black*

- The text color has been changed to black.

P4L95: *Please clearly define the hit efficiency and explain how it was calculated. It is also unclear what is meant by MASS and SIZE. Do these terms refer to the numbers of particles measured in the MASS and SIZE modes, respectively? Please provide a clear*

description of these operating modes and explain how they differ. In addition, please report the variability in the hit efficiency. Is 18.9% the maximum value? Please also provide the minimum and average values, together with an appropriate measure of variability, such as the standard deviation or range.

- Thank you for pointing out the lack of clarity in our description of the SPAMS detection efficiency. We have revised the Methods section to explicitly define the terms SIZE, MASS, and hit efficiency.

In the SPAMS measurement sequence, individual particles first pass through two 532 nm sizing lasers. Particles that produce valid scattering signals at both sizing lasers and for which a valid time-of-flight measurement is obtained are referred to as SIZE particles. Their measured velocity is used to determine the vacuum aerodynamic diameter (D_{va}) and to predict their arrival at the ionization region. The 266 nm desorption/ionization laser is then triggered, and particles that are successfully ionized and yield a valid mass spectrum are referred to as MASS particles. Thus, SIZE and MASS are not independent sampling modes, but represent sequential detection stages, with MASS particles forming a subset of the successfully sized particles.

The hit efficiency was calculated as

$$HE = \frac{N_{MASS}}{N_{SIZE}} \times 100\%,$$

where N_{MASS} and N_{SIZE} are the numbers of particles yielding valid mass spectra and valid sizing measurements, respectively.

These statistics have been added to Section 2.3 in the revised manuscript as follows.

“In the SPAMS detection sequence, particles first pass through two 532 nm continuous-wave sizing lasers. Particles producing valid scattering signals at both sizing lasers are recorded as successfully sized particles (hereafter referred to as SIZE particles), and their time of flight is used to determine the vacuum aerodynamic diameter (D_{va}). The measured particle velocity is then used to trigger the 266 nm ionization laser when the particle reaches the ion source. Particles that are successfully ionized and generate a valid mass spectrum are recorded as MASS particles. Thus,

SIZE and MASS do not represent two independent sampling modes; rather, they represent sequential stages of particle detection within the SPAMS measurement process, with MASS particles being a subset of the successfully sized particles. A total of 4,893,140 particles with valid bipolar mass spectra were retained for subsequent chemical analysis. The campaign-integrated hit efficiency was 18.9%, calculated as the ratio of the total number of MASS particles to the total number of SIZE particles.”

P4L95-96: *The authors refer to “number concentration” in the manuscript; however, the y-axis in Fig. S2 is labelled “Mass particle number.” Is the plotted quantity truly a particle number concentration (e.g., particles cm⁻³), or does it simply represent the number of particles detected in the MASS mode? I assume it is the latter. If the authors intend to report a number concentration, please explain clearly how it was derived from the SPAMS measurements, including any corrections, calibration procedures, sampling-flow information, detection-efficiency adjustments, or use of data from other reference instruments. Please use consistent terminology throughout the manuscript and clearly distinguish between particle number and particle number concentration wherever both quantities are discussed.*

- Thank you for pointing out this inconsistency. We agree that the quantity shown in Figure S2 was incorrectly described as a particle number concentration. The plotted SPAMS quantity represents the number of MASS particles detected within each synchronized sampling interval, rather than an independently calibrated ambient particle number concentration.

In the present study, no conversion of the SPAMS particle counts to an absolute number concentration (particles cm⁻³) was performed. Specifically, the MASS particle counts were not corrected using sampling-flow-derived sampled air volume, particle transmission efficiency, size-dependent detection efficiency, hit efficiency, or an external particle-number reference instrument such as a CPC or SMPS. Therefore, reporting these data in units of particles cm⁻³ would not be justified.

We have revised the manuscript accordingly. The term “particle number concentration” has been replaced by “particle number,” or “particle-number fraction,”

as appropriate. Figure S2 has also been revised so that the y-axis and caption clearly identify the plotted quantity as the number of MASS particles detected by SPAMS rather than a number concentration.

We further revised the semi-quantitative regression description to clarify that the SPAMS particle-number variable represents the detected MASS particle count within each synchronized time interval and not an ambient particle number concentration. Because the same detected particle-count variable was used in the original regression calculation, this terminology correction does not alter the numerical regression results.

Particle-number fractions used for comparing the four major classes and chemically resolved subclasses were calculated from the corresponding detected particle counts and are dimensionless relative quantities. We have revised the terminology throughout the main manuscript and Supplementary Information to clearly distinguish detected particle numbers, particle-number fractions, and semi-quantitatively estimated particulate nitrate mass concentrations.

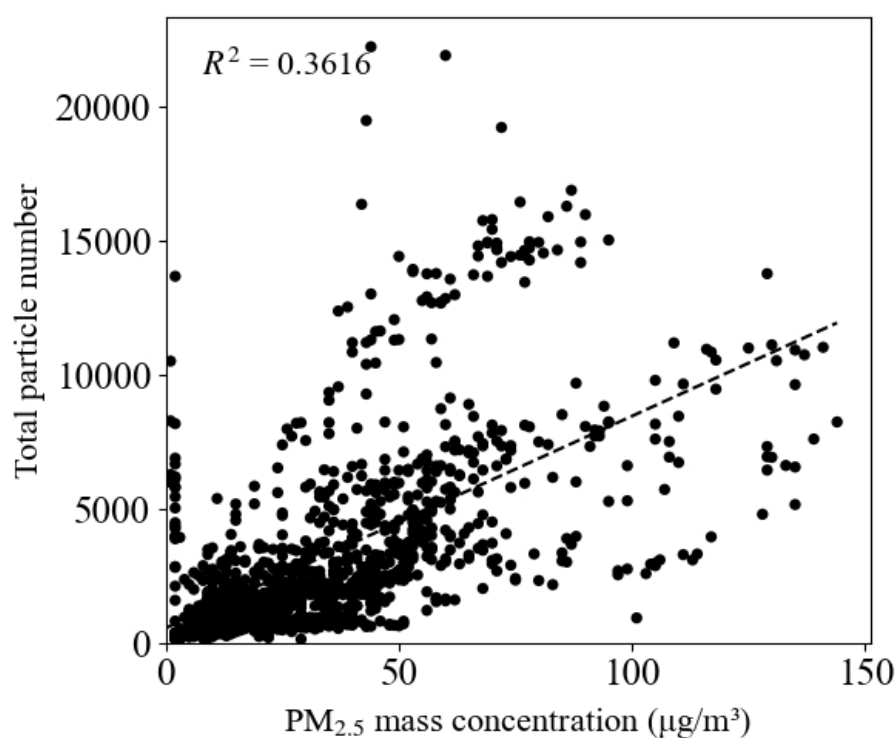
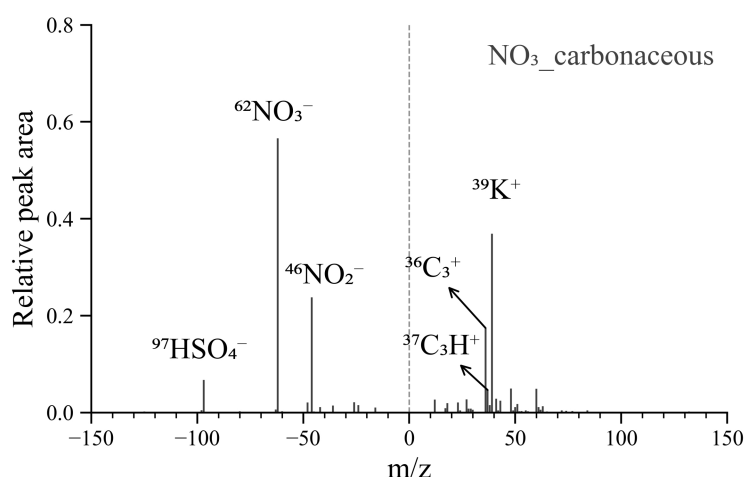


Figure S2. The correlation between particle number measured by SPAMS and PM_{2.5} mass loadings.

P5L149: $^{37}\text{C}_3\text{H}^+$ or $^{36}\text{C}_3 + ?$ I assume you mentioned the latter based on the spectra in Fig 1a. Please add the corresponding m/z values for all the organic fragment ions mentioned in the manuscript, as has been done for the other fragment ions, to maintain consistency.

- Thank you for identifying this error. The intended ion is C_3^+ at m/z 36, consistent with the mass spectrum. We have corrected the text and added the corresponding m/z values for all organic fragment ions throughout the manuscript for consistency.



P7L165: “Figure S11” do you mean S12?

- This was an incorrect figure reference and has been corrected to **Figure S14**.

P7L167: Please use “nitrate mass concentration” instead of “mass concentration” throughout the manuscript. The latter may be misinterpreted by readers as referring to the total particle mass concentration, whereas the quantity presented is specifically the nitrate mass concentration.

- “Mass concentration” has been replaced with “nitrate mass concentration” wherever the quantity specifically represents particulate nitrate rather than total particle mass.

P9L220 -P10L229: Please remove all the “(positive)” and “(negative)”, which are redundant.

- Thank you for the suggestion. We agree that the terms “(positive)” and

“(negative)” are redundant because the ion polarity is already indicated by the ionic charge notation. These expressions have been removed in the revised manuscript. In addition, this section has been substantially reorganized following consolidation of the original 12 particle categories into seven chemically resolved subclasses

P9L221: Change “No3_K_S” to “NO3_K_S”

- The former NO3_K_N, NO3_K_S, and NO3_K_CN groups have been combined into a single NO3_K-rich subclass.

P10L227-229: *The statement “chloride–nitrate replacement in aged sea-salt particles” is not supported by the evidence presented in the manuscript. Please either provide clear evidence to support this interpretation or revise the statement to a more appropriate and evidence-based description.*

- This statement has been removed. The revised manuscript does not infer chloride–nitrate replacement from Na-rich nitrate spectra in the absence of independent evidence demonstrating an original sea-salt composition.

P10L233: *Elevated levels of NO3_NaK cannot suggest contributions from sea salt.*

- The interpretation of elevated NO3_NaK as evidence for sea-salt contribution has been removed. Following the revised classification, these particles are included in the broader Na-rich nitrate-containing subclass without assignment to a unique source

P11L251-252: *Refer to major comment #4, please remove the sea salt related sentence or revise.*

- The sea-salt interpretation has been removed. The temporal variation is now discussed only in terms of changes in the abundance of Na-rich nitrate-containing particles.

P13L301-305: *Refer to major comment #4, please remove the sea salt related sentence or revise.*

- The discussion attributing the coarse Na-rich particles to sea salt and chloride replacement has been removed. The size-dependent enrichment is now described observationally as an enhancement of Na-rich nitrate-containing particles at larger particle sizes, without assigning a specific source.

P15L330: *It generally cannot be concluded "chloride depletion" from the absence of Cl⁻ alone.*

- The statement concerning chloride depletion has been removed. Low or absent Cl⁻ signals are no longer used as evidence for chloride displacement or a sea-salt origin

P15L332: *I cannot see the shaded areas for the PEs in Fig S13*

- The pollution episodes have been made clearly visible in the revised figure using labeled intervals (PE1–PE4), and the figure caption has been revised accordingly.

P15L332: *I cannot see NO₃ Na-rich peak during PE1*

- Thank you for pointing this out. We have rewritten the section.

P17 Fig7: *Please ensure that the color coding is consistent across the legends in all panels. Once the color scheme is made consistent, a single shared legend should be sufficient. For example, the 4.17% entry should use the same color in every panel, rather than being yellow in EP1 and EP3 but purple in EP2 and EP4.*

- Thank you for pointing out the potential ambiguity in the color coding of Figure 7. We would like to clarify that the percentages shown in the legends represent the occurrence frequencies of the trajectory clusters within each individual pollution episode, whereas the colors are used to distinguish the independently resolved trajectory clusters within each panel.

The trajectory clustering was performed separately for PE1–PE4. Therefore, clusters in different panels are not necessarily equivalent in transport direction, origin, or trajectory characteristics, even when they happen to have the same occurrence frequency. For example, a cluster contributing 4.17% in PE1 is not necessarily the same

trajectory cluster as a 4.17% cluster in PE2 or PE4. Thus, assigning the same color solely on the basis of an identical percentage could incorrectly imply correspondence between independently derived clusters. Because the clusters are episode-specific rather than directly corresponding across PE1–PE4, separate panel legends are retained rather than using a single shared legend.

P19L422: change “mass” to “mass of particulate species”

- We have rewritten the section of Conclusions and Atmospheric Implications

Fig1: Panel (a), add 36 next to C3 + ; the arrows for 62NO3 - and 16O- should not be so straight, as they cover the actual peaks; the label 46NO2 - should be moved to the right to avoid overlapping with the m/z 62 peak. Panel (b) for the NO3_OCEC type, where are the EC marker peaks in the mass spectra? I do not observe a clear $C_n^{\pm}$ patterns, similarly for NO3_EC in FigS12. Please re-examine the spectra and verify whether this classification is appropriate. Consider providing zoomed-in views of the relevant m/z ranges to better highlight any characteristic ion patterns, if present. This would make the spectral features easier to identify and support the corresponding interpretation. In the figure caption, please mention the number of spectra used for each averaged spectrum. Keep the y-axis scale consistent (both ranges and the intervals) across all panels to facilitate direct comparison.

- We have revised the Figures (Figure 1 and Figure S15) in the revised manuscript and supplementary materials as follows.

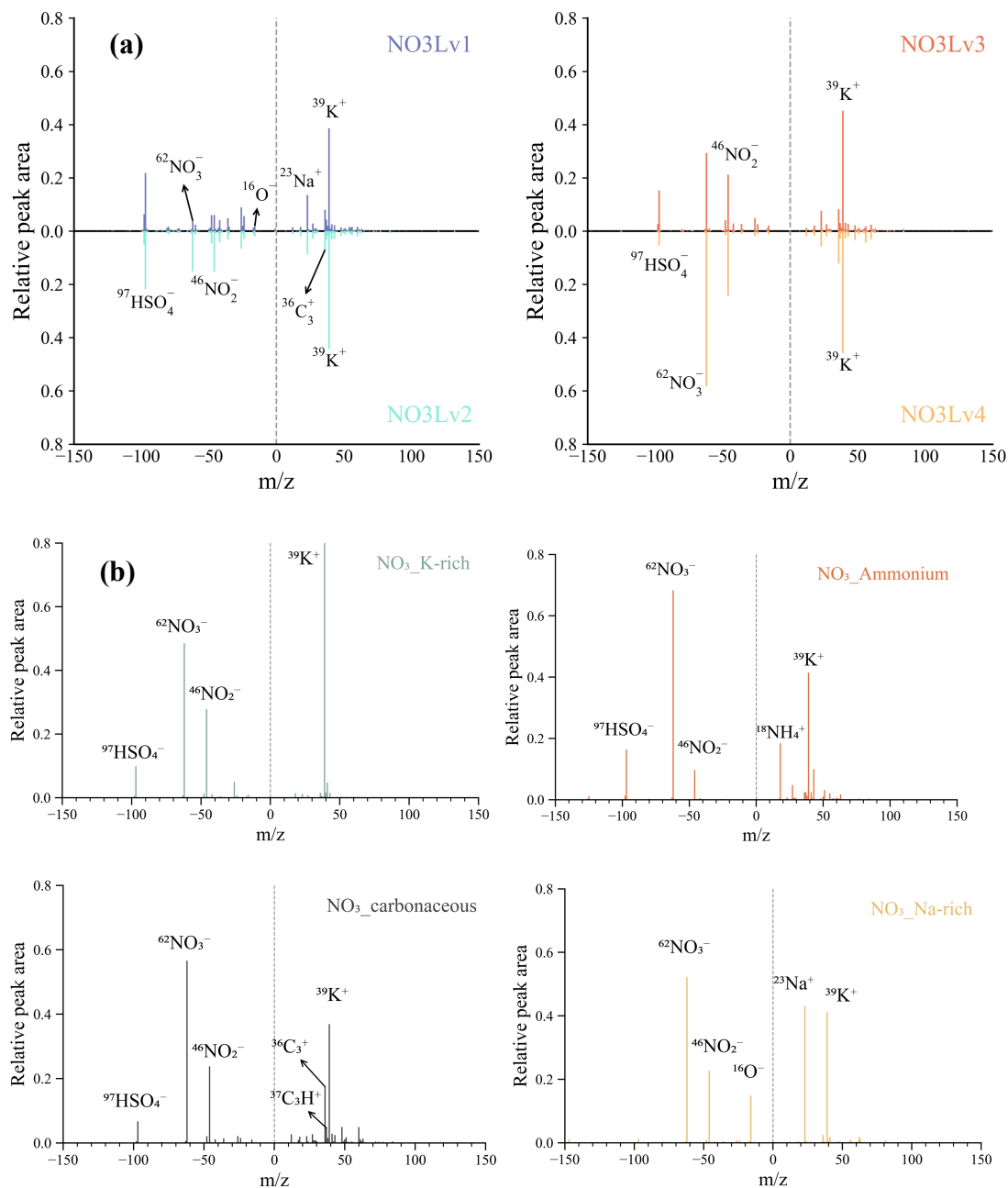


Figure 1: The average single-particle mass spectra for (a) four nitrate-containing particle classes (NO₃Lv1, NO₃Lv2, NO₃Lv3, and NO₃Lv4), and (b) nitrate-containing particle subclasses (NO₃_K-rich, NO₃_carbonaceous, NO₃_Na-rich derived from NO₃Lv4 cluster analysis). The x-axis is the mass-to-charge ratio (m/z), and the y-axis is the relative peak area (normalized intensity). Positive values correspond to cation signals and negative values to anion signals, indicating the relative importance of each ion within that particle type. Characteristic marker ions are labeled, including K⁺ (m/z

39), Na^+ (m/z 23), organic fragment ions such as C_3H^+ (m/z 37) and C_3^+ (m/z 36), and anions such as NO_3^- (m/z 62), NO_2^- (m/z 46), and HSO_4^- (m/z 97).

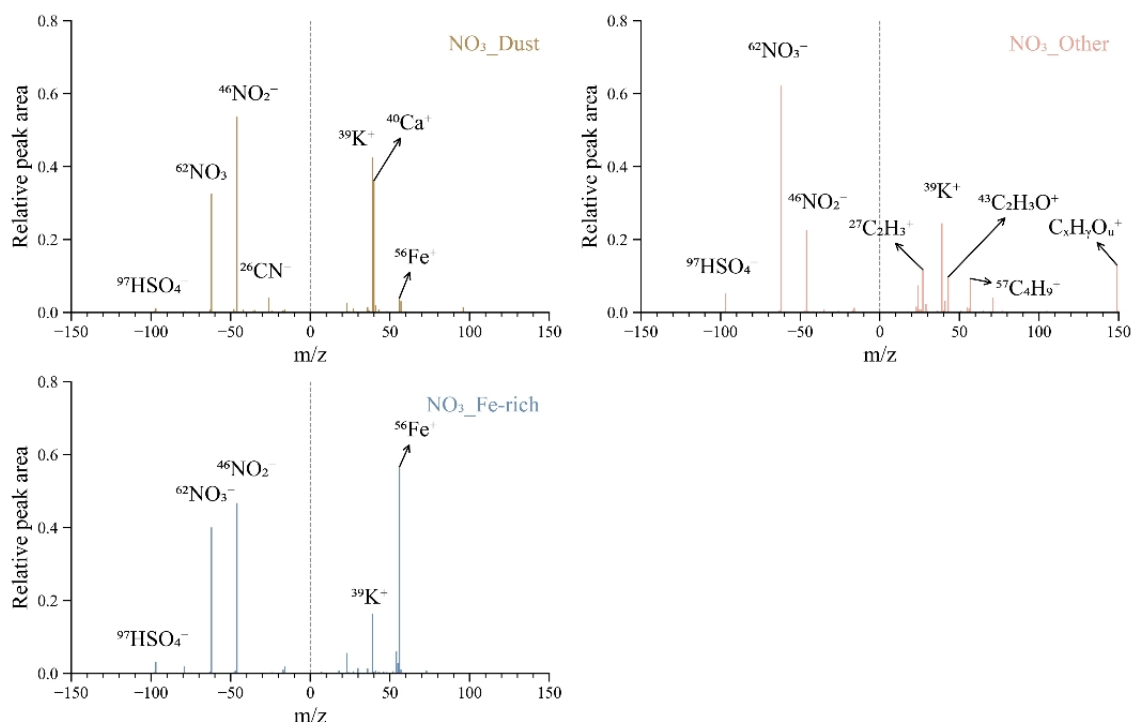


Figure S15. Representative mass spectra of eight additional nitrate-containing particle subclasses identified by SPAMS, including **NO3_Dust**, **NO3_Fe-rich**, and **NO3_Other**. Positive ion spectra are shown on the right side of the vertical dashed line, and negative ion spectra are shown on the left side. Together with the spectra shown in Figure 1b, these spectra provide representative spectral evidence for all 7 nitrate-containing particle subclasses.

Fig2: Please use the same scale for all upper panels and, separately, the same scale for all lower panels to facilitate comparison. In addition, please relabel the lower panels from a–d to e–h to avoid confusion with the upper panels. Please use “nitrate mass concentration” instead of “mass concentration”. The latter may be misinterpreted by readers as referring to the total particle mass concentration.

- We have modified the Figure 2 as follows.



Figure 2: Diurnal patterns of particle number and nitrate mass concentrations for four nitrate-containing particle classes. The solid line shows the average value as a function of local time (Hour of Day, 0–24 h), and the shaded area represents the variability (25th and 75th percentiles).

Fig3: Please use “nitrate mass concentration” instead of “mass concentration”.

- We have modified the Figure 3 as follows.

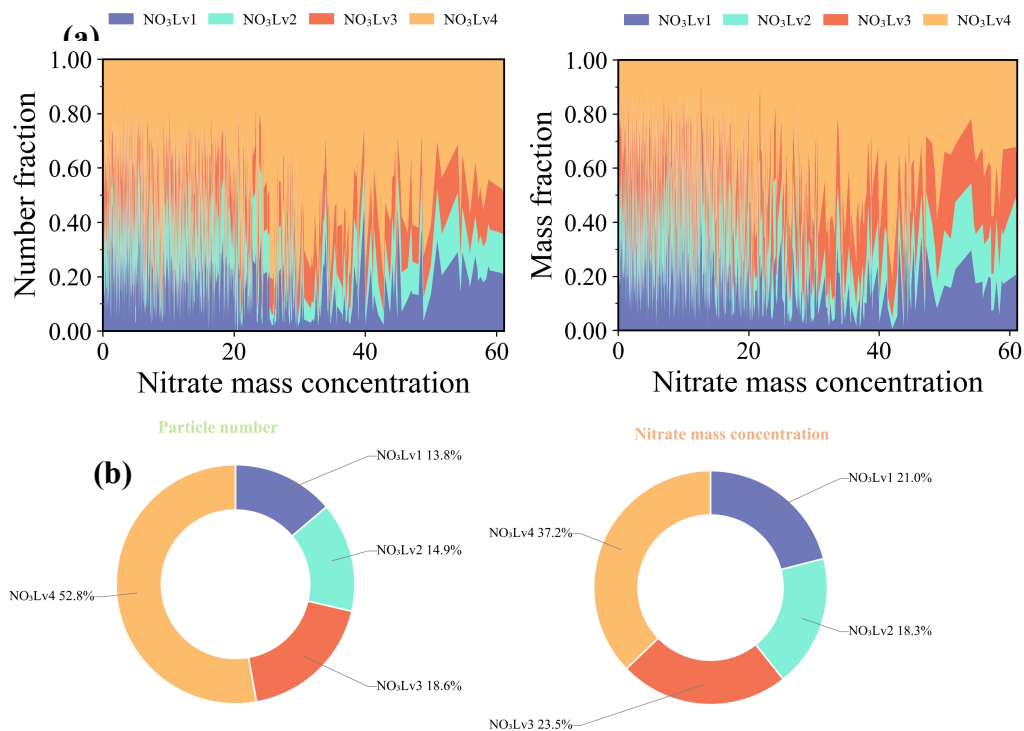


Figure 3: (a) The variation of particle number and nitrate mass concentrations for four nitrate-containing particle classes as a function of nitrate mass concentration during the whole observation period. (b) The average fractions of four nitrate-containing

particle classes in particle number and nitrate mass concentrations.

Fig6: Please use “nitrate mass concentration” instead of “mass concentration”; Please show the pollution episodes with labels PE1, 2, 3... in the time series. Consider moving this figure to the supplement.

- We have modified the Figure 6 as follows.

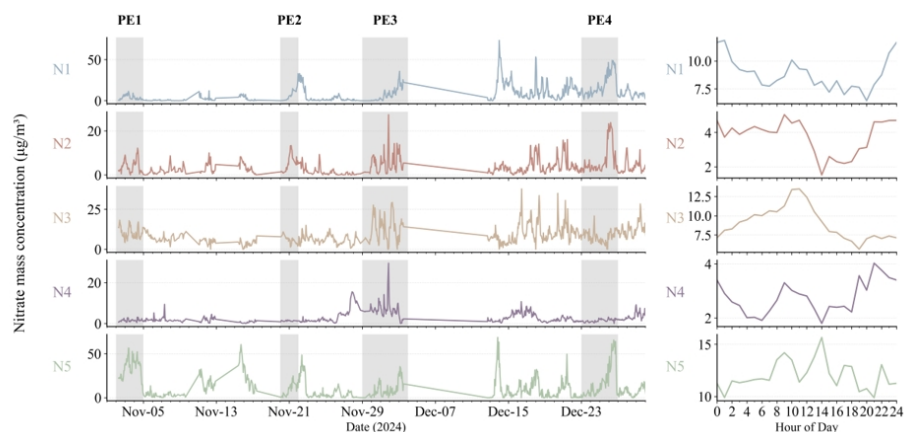


Fig S1: The measurement site seems to be in the lake. If yes, please mention. If not, please correct the location. Change “sites” to “site”.

- We have revised the caption and Figure S1 as follows.



Figure S1. Location of observation site in Shanghai. The base map is from © Google Maps 2025.

Fig S2: The y-axis label, "Mass particle number," is unclear. Please define exactly what this quantity represents. In the manuscript, the authors also refer to "number concentration." Is this truly a number concentration (e.g., particles cm^{-3}), or is it simply the number of particles detected in the MASS mode? Please use consistent terminology throughout the manuscript and clearly distinguish between particle number and number concentration, if both quantities are reported. Please give the R^2 value.

- We have modified the description throughout the manuscript and changed the y-axis label as follows.

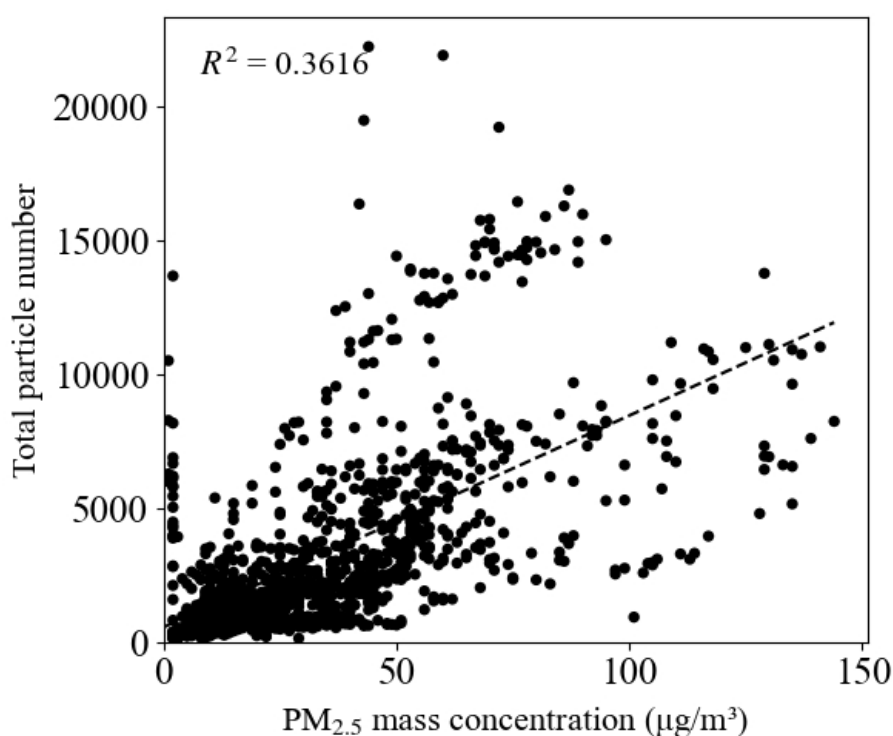


Figure S2. The correlation between total particle number measured by SPAMS and PM_{2.5} mass loadings.

Fig S12: In the figure caption, please mention the number of spectra used for each averaged spectrum. Keep the y-axis scale consistent (both ranges and the intervals) across all panels to facilitate direct comparison.

- It turns out that Figure S12 has become Figure S15 in the current manuscript. We have followed the reviewer's suggestion to "Keep the y-axis scale consistent (both ranges and intervals) across all panels to facilitate direct comparison."

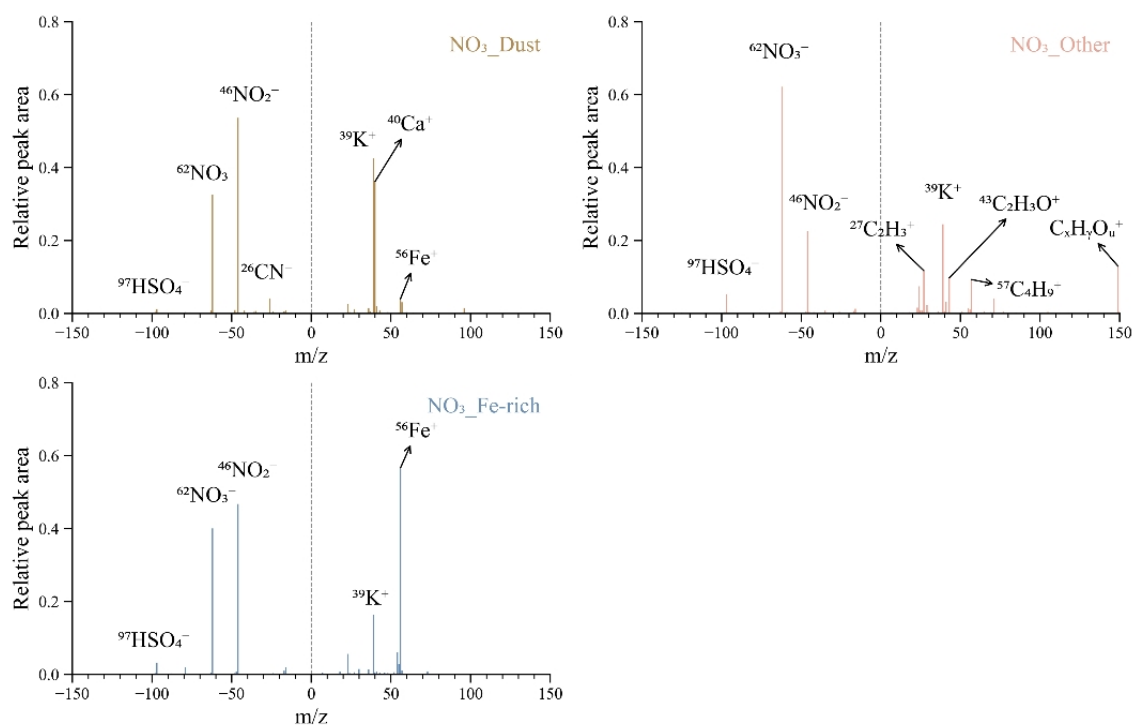
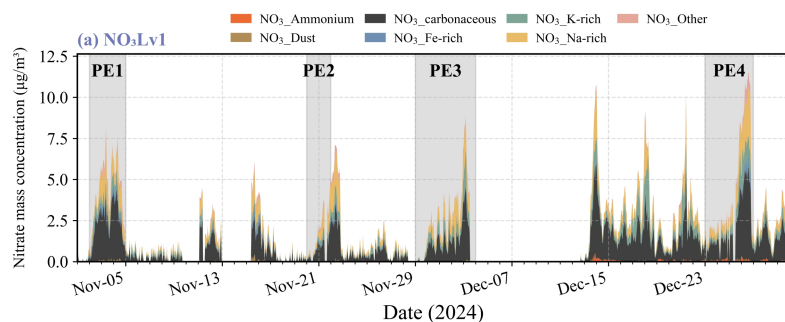


Figure S15. Representative mass spectra of eight additional nitrate-containing particle subclasses identified by SPAMS, including *NO3_Dust*, *NO3_Fe-rich*, and *NO3_Other*. Positive ion spectra are shown on the right side of the vertical dashed line, and negative ion spectra are shown on the left side. Together with the spectra shown in Figure 1b, these spectra provide representative spectral evidence for all 7 nitrate-containing particle subclasses.

Fig S13: There are two Fig S13, please correct the number. Please show the pollution episodes with labels PE1, 2, 3... in the time series

- We have added the pollution episodes with labels PE1,2,3....in the time series as follows.



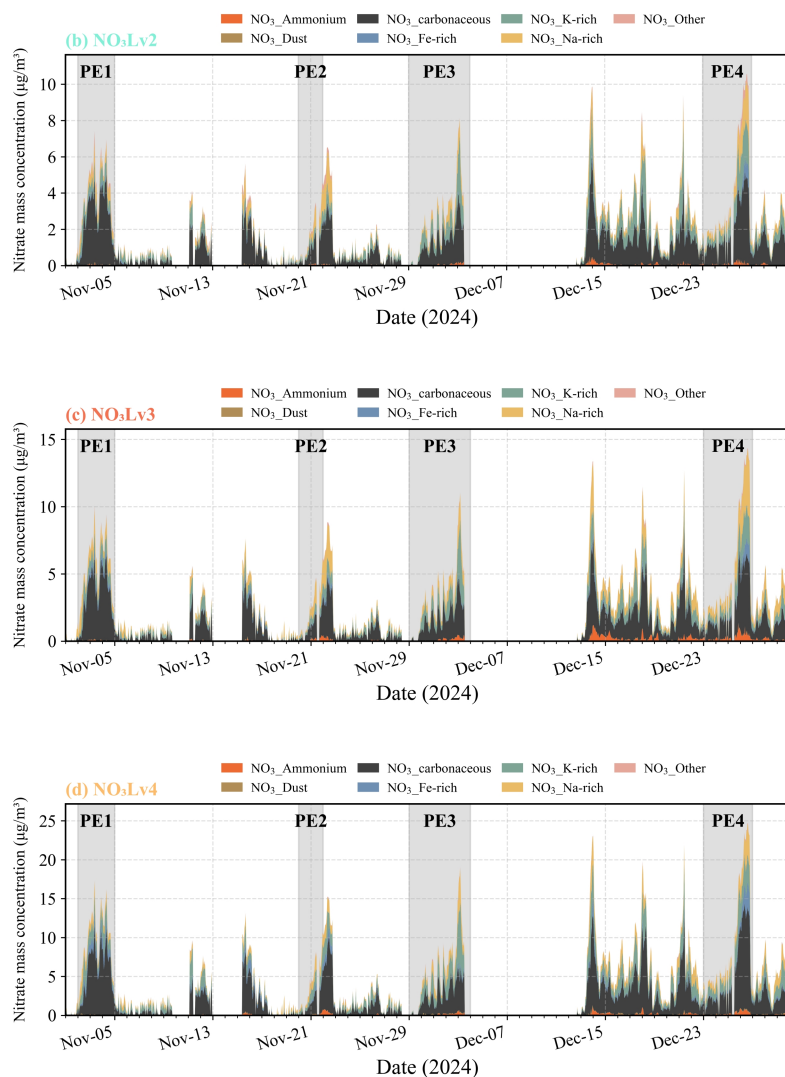
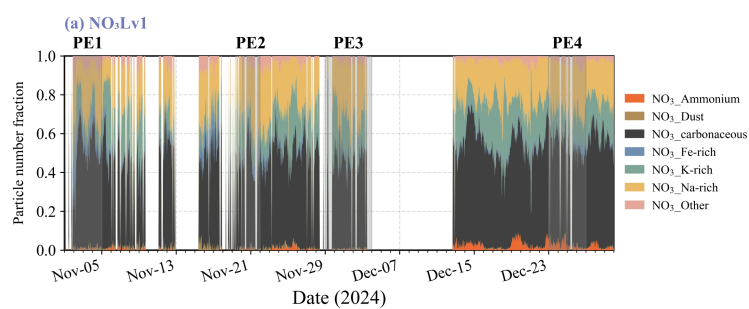


Figure S16. Time series of particulate nitrate mass contributions of the seven chemically resolved subclasses within (a) NO₃Lv1, (b) NO₃Lv2, (c) NO₃Lv3, and (d) NO₃Lv4 over the sampling period.



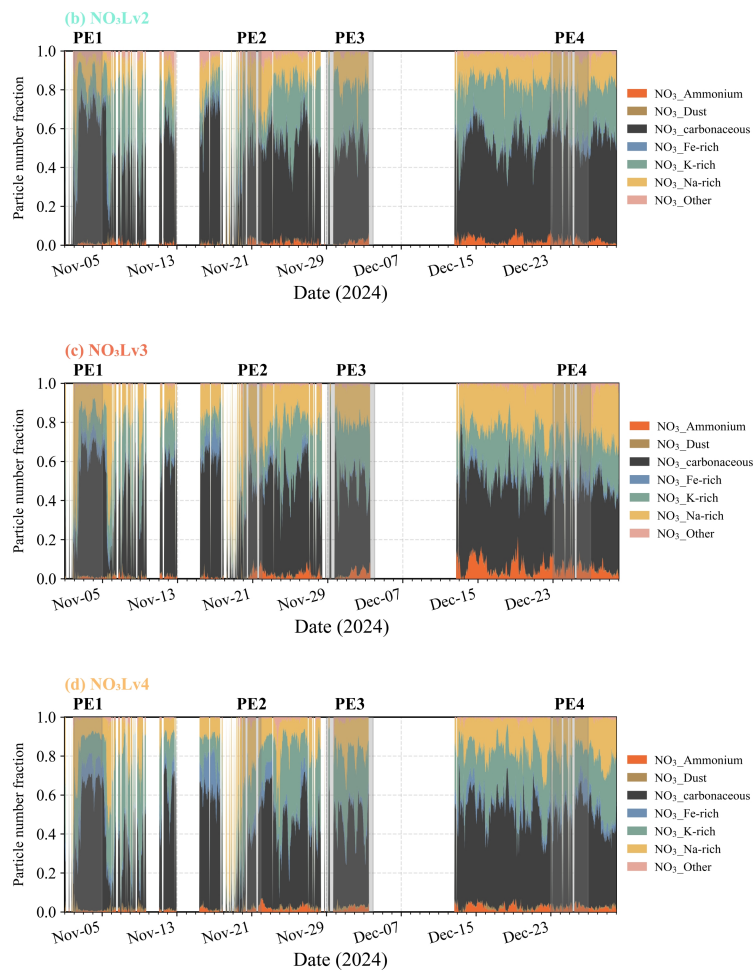


Figure S17. Time series of particle-number fractions of the seven chemically resolved subclasses within (a) NO3Lv1, (b) NO3Lv2, (c) NO3Lv3, and (d) NO3Lv4 over the sampling period.

Fig S15: Refer to major comment #3

- In response to Comment 3, we have redrawn Figure S15 from the original manuscript; in the current revised version, this figure is presented as Figure S18.

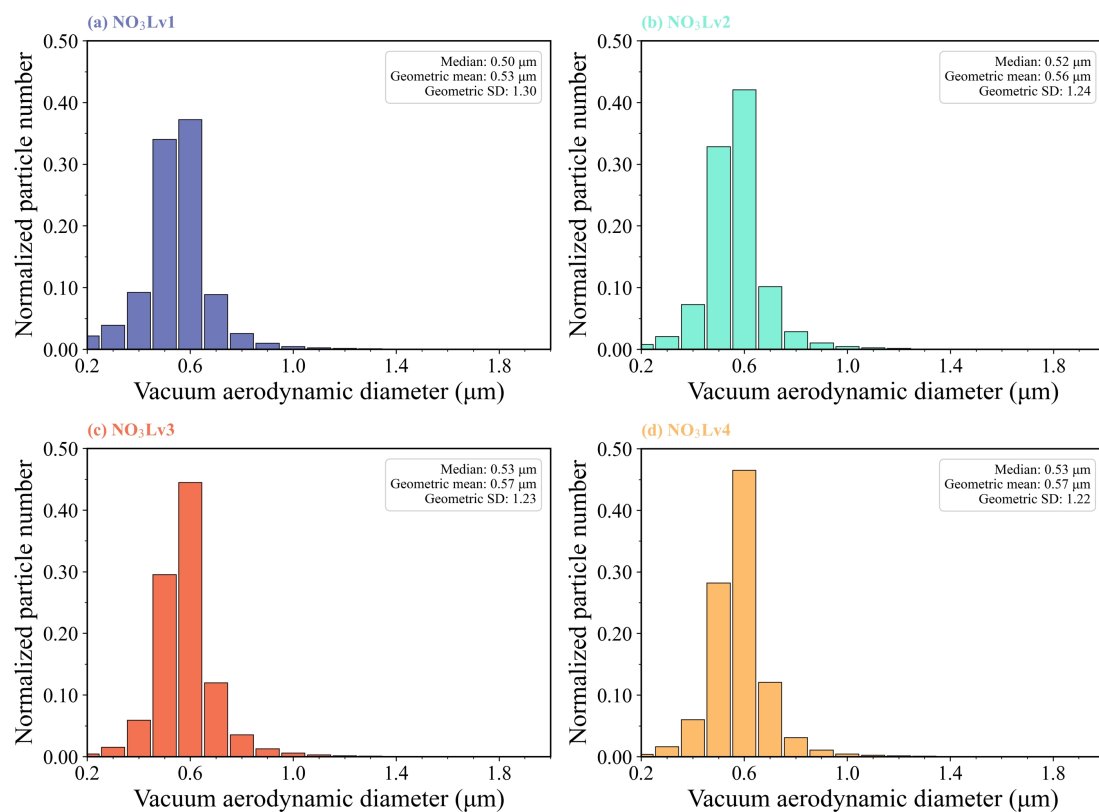


Figure S18. Size-resolved number fraction of nitrate-containing particle classes during the whole observations.