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

General comments

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 semi-quantitative 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 semi-quantitative 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**.

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.

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.

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 "nitrate-containing 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.

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.

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.

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.

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.

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.

P1L17: Is the 0.5-0.7 um Dp or Da or Dva? The particle sizes reported by SPAMS are typically vacuum aerodynamic diameters (Dva), not physical diameters (Dp). Unless the authors have converted the measurements to physical diameters, please replace Dp with Dva (or clearly define the diameter metric used) throughout the manuscript.

P1L20: Please remove the term "chloride-depleted sea salt," as no evidence is presented to support this interpretation.

P1L24-26: The results cannot indicate NOx-NH3 chemistry, please revise.

P3L71: *Dp* 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 (*Da* or *Dva*) throughout the manuscript to avoid confusion.

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.

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.

P3L84: Add "(CO)" after carbon monoxide to keep consistency.

P4L93: Change the color of "the" 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.

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.

P5L149: $37C_3H^+$ or $36C_3^+$? I assume you metioned 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.

P7L165: "Figure S11" do you mean S12?

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.

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

P9L221: Change "No3_K_S" to "NO3_K_S"

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.

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

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

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

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

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

P15L332: I cannot see NO3_Na-rich peak during PE1

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.

P19L422: change "mass" to "mass of particulate species"

Fig1: Panel (a), add ^{36} next to C_3^+; the arrows for $62NO_3^-$ and $16O^-$ should not be so straight, as they cover the actual peaks; the label $^{46}NO_2^-$ 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.

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.

Fig3: Please use "nitrate mass concentration" instead of "mass concentration".

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.

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

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.

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.

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

Fig S15: Refer to major comment #3