

Response to comments

Reviewer 1

Comments:

The manuscript deals with barium containing aerosols originating from fireworks, addressing chemical alteration and the related health effects. Combination of single-particle analysis with monitoring of metal content and concentration of ionis species in PM_{2.5} fraction provides comprehensive information on barium containing particles.

We sincerely thank the reviewer for the constructive and insightful comments on our manuscript. We have carefully considered all the points raised and revised the manuscript accordingly. All modifications are highlighted in blue in the marked manuscript and the marked Supplement. Clean revised versions are also provided. Our point-by-point responses to each comment are provided below.

General comments

1. Ageing and mixing state of Ba-containing aerosol particles is well addressed and discussed based on combined data set of single-particles and bulk analyses. However, health effects are estimated using simple calculations based on average Ba concentrations of PM_{2.5} and seems to be a marginal part of the manuscript.

We thank the reviewer for this comment. We agree that the health effects analysis was relatively brief and based on simplified calculations using mean Ba mass concentrations, and that it appears as a marginal part of the manuscript.

As the reviewer correctly noted, the primary focus of this study is the atmospheric aging mechanisms and mixing states of firework-derived Ba-containing particles, supported by the combined dataset of single-particle and bulk analyses. Given this focus, the health-related analysis is intentionally presented as a supplementary context rather than a core component of this study.

To ensure that this supplementary role is clearly communicated to readers, we have revised the manuscript as follows:

(1) **Abstract:** We have added a brief statement on health implications in the abstract: "Screening-level hazard quotients (HQs) based on an oral reference dose (RfD) surrogate were below 1, but short-duration Ba concentration peaks warrant further evaluation of their potential inhalation-related health implications using inhalation-specific toxicity benchmarks." Please refer to Lines **28–30** of the revised manuscript.

(2) **Section 2.5 (Field measurements):** The title has been changed from "Health risk assessment" to "Preliminary exposure and risk assessment methodology" to clearly indicate the preliminary nature of this methodology. In addition, we have added a clear statement that the oral RfD is used as a surrogate in the absence of an established inhalation RfC for Ba, and we have expanded the uncertainty discussion to include chemical speciation, solubility, and bioavailability.

"As no inhalation reference concentration (RfC) is available for Ba, the oral reference dose (RfD) was used as a surrogate. We acknowledge that this substitution may introduce uncertainty regarding inhalation-specific bioavailability." has been added to the revised manuscript. Please refer to Lines **132–134** of the revised manuscript.

(3) **Section 3.4 (Results and discussion):** The title has been changed from "Health effects of Ba from fireworks" to "Preliminary exposure and risk assessment" to more accurately reflect the scope of this analysis, as our study did not directly measure health effects.

(4) **Conclusions:** In the Conclusions section, we have retained only a brief statement on the health implications, which now reads: "Fourth, although all screening-level HQ estimates based on an oral RfD surrogate were below 1, peak Ba concentrations during firework events were 1–3 orders of magnitude above background levels, warranting further assessment of their potential inhalation-related health implications." This formulation uses more neutral language ("implications" rather than "impacts") and reflects the supplementary role of this analysis. Please refer to Lines **338–341** of the revised manuscript.

2. The abstract should reflect the manuscript content, however the estimation of health effects are not even mentioned in it.

We thank the reviewer for pointing this out. We have added a brief summary of the health implications at the end of the abstract, as an extended background of the study significance:

"Screening-level hazard quotients (HQs) based on an oral reference dose (RfD) surrogate were below 1, but short-duration Ba concentration peaks warrant further evaluation of their potential inhalation-related health implications using inhalation-specific toxicity benchmarks." has been added to the revised manuscript. Please refer to Lines **28–30** of the revised manuscript.

Specific comments

3. Abstract, 1.17-19: The authors state: "The highest concentrations occurred in restricted zones rather than the more densely populated urban core, demonstrating the effectiveness of local restriction policies." As such, the sentence seems to be contradictory. It should be mentioned that fireworks are prohibited in the urban core.

We thank the reviewer for pointing this out. We agree that the original sentence appeared contradictory because the distinction between firework-prohibited and firework-restricted areas was not clearly explained. We have therefore revised the abstract to clarify that fireworks were completely prohibited in the urban core, whereas they were permitted in the restricted zones only at designated times and locations. The revised sentence now reads:

"Peak Ba concentrations varied substantially among sites. Despite its substantially higher population density, the urban-core site under a complete firework ban exhibited a lower peak Ba concentration than a suburban site with time- and location-restricted firework use. This contrast was consistent with a potential mitigating influence of stricter controls, although site-specific emissions and transport may also have contributed." has been added to the revised manuscript. Please refer to Lines **18–21** of

the revised manuscript.

4. Figure 1 panel (c) 1. 290. Size distributions are usually lognormal. Number size distribution of Ba containing particles should be plotted as $dN/d\log D$. The same comment is valid for Figure S5 panel (b) and Figure S6 in Supplement.

We thank the reviewer for this comment. Following the reviewer's recommendation, we have replotted Figure 1c and Figure S5b using $dN/d\log D$ as the y-axis and set the x-axis to a logarithmic scale to properly display the lognormal characteristics of the size distributions. The figure captions have been revised accordingly.

For Figure S6, which presents the relative number fractions of different particle types across size bins (stacked bar chart) rather than a number size distribution curve, we have retained the linear x-axis. Unlike the size distribution curves (Figs. 1c and S5b), which require logarithmic scaling to represent lognormal distributions correctly, Figure S6 is intended to show compositional differences across discrete particle size bins. Given that the stacked bars represent discrete size intervals rather than a continuous distribution, a linear scale is appropriate for this type of presentation. The use of a linear scale in this specific case does not affect the interpretation of the relative fractions and is consistent with common practice for stacked bar charts in single-particle studies. We have revised the figure caption to more accurately reflect the content, changing it from "size distribution" to "relative number fractions by particle size."

The revised Figures 1, S5 and S6 are as follows:

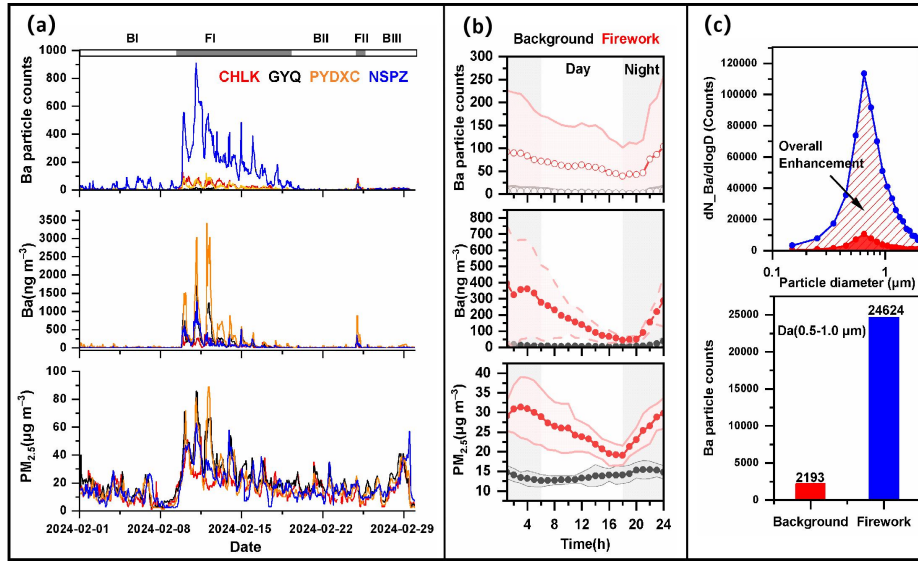


Figure 1. Temporal variations and size distributions of particulate matter. (a) Time series of $PM_{2.5}$ mass concentration, Ba mass concentration, and Ba-containing particle counts at the four sites (firework periods shaded), respectively. (b) Diurnal patterns of $PM_{2.5}$ mass concentration, Ba mass concentration and Ba-containing particle counts at the four sites during firework periods (red) and background periods (black). (c) Upper panel: particle size distributions of Ba-containing particles (plotted as $dN_{Ba}/d\log D$); lower panel: comparison of total Ba-containing particle counts in the 0.5–1.0 μm size range between background and firework periods.

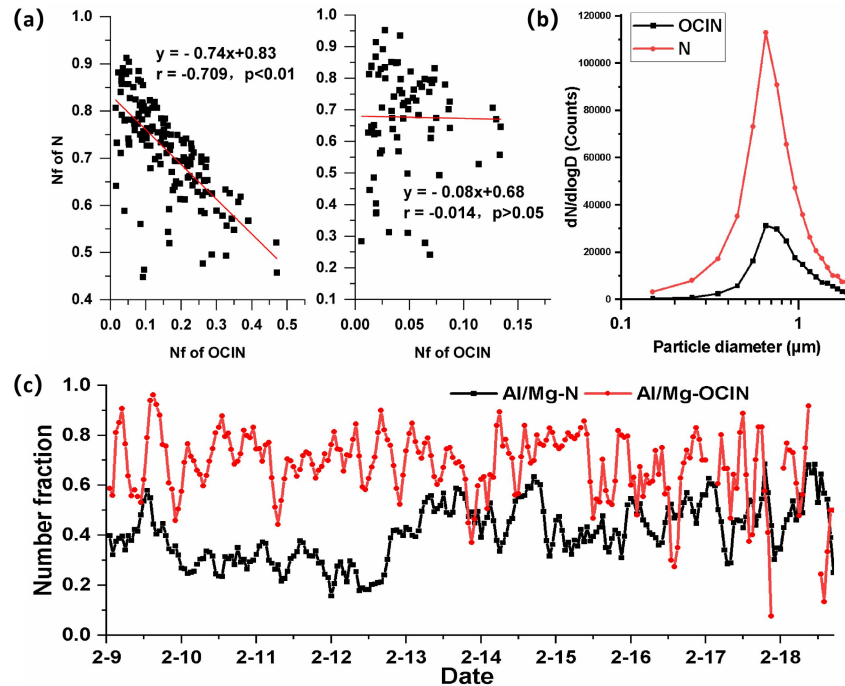


Figure S5. N and OCIN particle characteristics at the four sites during FI. (a) Correlation between the relative number fractions (Nf) during 9–15 February (left) and 16–19 February (right); (b) Particle size distributions of N and OCIN particles (plotted as $dN/d\log D$); (c) Time series of Al- or Mg-containing fractions in N and OCIN particles (3-hour moving average applied).

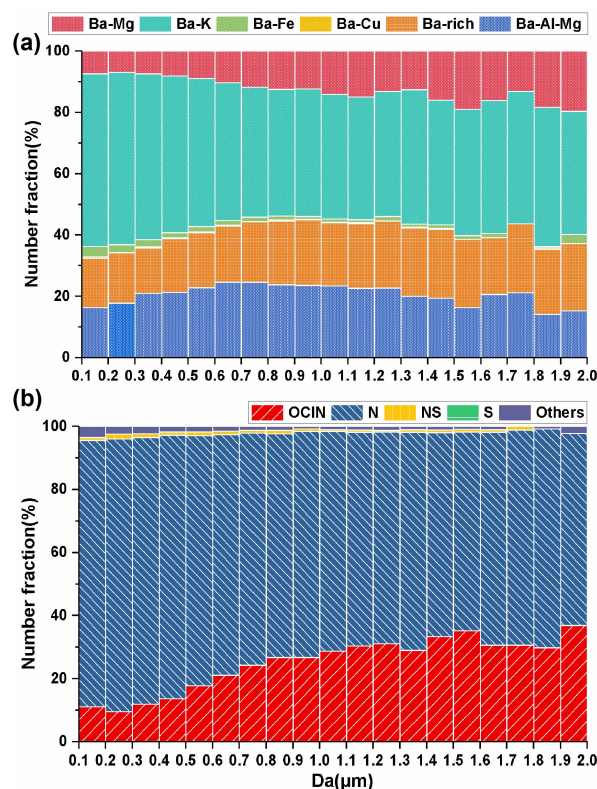


Figure S6. Relative number fractions of the main types of Ba-containing particles by particle size at the NSPZ site. (a) Classification based on positive ion mass spectra; (b) Classification based on negative ion mass spectra.

Technical comments

5. Health risk assessment, l. 116: Equations should be independent on the units of measure, "(mgkg-1day-1)" should be moved to the definition of D_{inh} in l.115.

We thank the reviewer for this correction. We have moved the unit "(mg·kg⁻¹·day⁻¹)" from the equation to the definition of D_{inh} , so that the equation is now independent of the units of measure.

"The average daily exposure dose (D_{inh} , mg·kg⁻¹·day⁻¹) was calculated as following the USEPA framework adapted from Kong et al. (2015), with period-specific parameters:" has been added to Section 2.5. Please refer to Lines 134–136 of the revised manuscript.

6. Figure 1, 1.290: "Number of Ba" should be clarified.

We thank the reviewer for pointing this out. We agree that "Number of Ba" was ambiguous. To clarify, we have revised the label to "Ba particle counts" in the figure and updated the figure caption accordingly to explicitly indicate that the values represent the number of Ba-containing particles detected by SPAMS.

The revised Figure 1 and its caption are as follows:

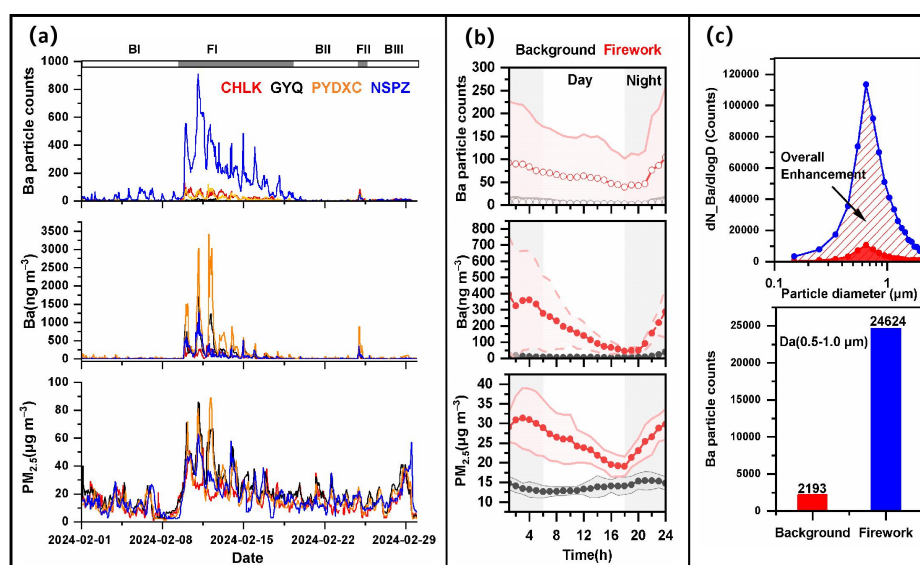


Figure 1. Temporal variations and size distributions of particulate matter. (a) Time series of PM_{2.5} mass concentration, Ba mass concentration, and Ba-containing particle counts at the four sites (firework periods shaded), respectively. (b) Diurnal patterns of PM_{2.5} mass concentration, Ba mass concentration and Ba-containing particle counts at the four sites during firework periods (red) and background periods (black). (c) Upper panel: particle size distributions of Ba-containing particles (plotted as dN_{Ba}/dlogD); lower panel: comparison of total Ba-containing particle counts in the 0.5–1.0 μm size range between background and firework periods.

7. Supplement, Figure S1: Secondary Y axis title "Mass" is erroneous, should read "Number of Ba-containing particles"

We thank the reviewer for this comment. The secondary Y-axis in Figure S1 was originally labeled "Mass" which was incorrect. The intended variable was the total number of particles detected by SPAMS across all chemical types, not the number of Ba-containing particles. We have therefore revised the label to "Total detected particle counts" to accurately reflect the data shown. The figure caption has been updated

accordingly.

The revised Figure S1 and its caption are as follows:

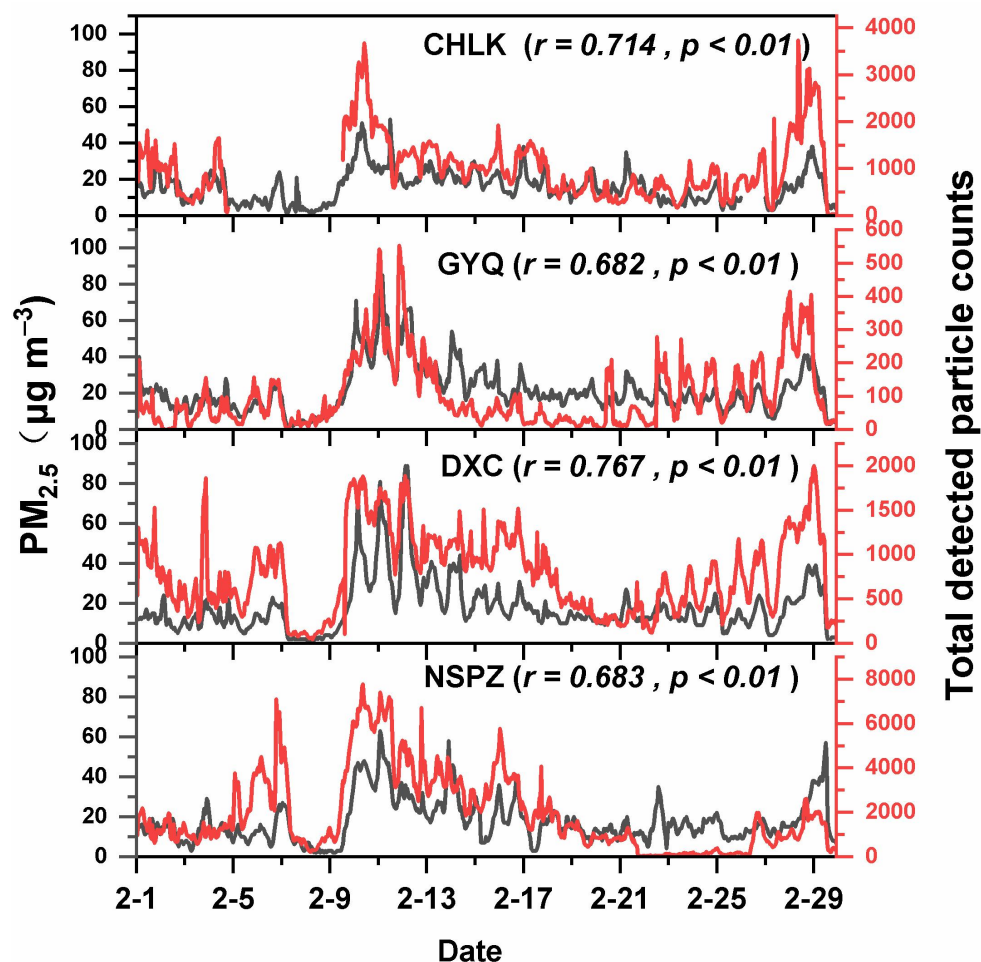


Figure S1. The time series and correlations of total detected particle counts and PM_{2.5} mass concentration at the four sites, respectively.

8. Figure S4: Barium as the element of interest is missing from the plot.

We thank the reviewer for this comment. We agree that the Ba time series is not shown in Figure S4. As the full Ba time series is already presented in Figure 1a of the main text, we considered that adding it to Figure S4 would risk duplicating the main text. Instead, we have added a note in the Figure S4 directing readers to Figure 1a for the Ba data.

The revised caption now reads:

"Figure S4. Synchronous time curves of potassium ion (K⁺), chloride ion (Cl⁻), copper (Cu), lead (Pb), nitrate (NO₃⁻), sulfate (SO₄²⁻), NO₂, and SO₂ mass concentrations at

the four sites, respectively. The time series of Ba mass concentrations is presented in Figure 1a of the main text."

9. Figure S6, caption: "The relative number fractions and size distribution of the main types of Ba-containing particles." Size distribution is not plotted just relative number fractions of the main types of Ba-containing particles in each size bin.

We thank the reviewer for this correction. We agree that the original caption was imprecise. Figure S6 displays the relative number fractions of the main types of Ba-containing particles in each size bin, rather than a separate size distribution. We have revised the caption accordingly to: "Figure S6. Relative number fractions of the main types of Ba-containing particles by particle size at the NSPZ site. (a) Classification based on positive ion mass spectra; (b) Classification based on negative ion mass spectra."