Response to comments

Reviewer 2

Comments:

The manuscript presents field observations of firework-related Ba-containing aerosols in Guangzhou during the Chinese Spring Festival and Lantern Festival. By combining online metal measurements, water-soluble ions, gaseous pollutants, and single-particle aerosol mass spectrometry, the authors examine the temporal variation, spatial heterogeneity, mixing state, and possible aging pathways of Ba-containing particles. The topic is important and relatively underexplored, and the multi-site single-particle dataset is valuable for understanding the atmospheric processing of firework-derived metal aerosols. I recommend minor revision. However, several conclusions should be interpreted more cautiously, as detailed below:

We thank the reviewer for the positive assessment of our work. We are encouraged by the recognition that our topic is important and that our dataset is valuable. In response to the reviewer's suggestion that several conclusions should be interpreted more cautiously, we have thoroughly re-examined our statements and revised the relevant sections accordingly. Detailed responses to each specific comment are provided below.

1. The interpretation of nitrate enrichment as evidence of atmospheric aging needs clarification. Fireworks commonly contain nitrate-based oxidizers, such as KNO_3 or $Ba(NO_3)_2$, which may directly emit primary nitrate-containing particles during combustion. Thus, the increase in nitrate-rich particles cannot be attributed solely to secondary nitrate formation or chloride-to-nitrate conversion. The authors should better distinguish primary nitrate emissions from secondary nitrate produced during post-emission aging. Analyses of the temporal relationships among K^+, Ba, Cl^-, and NO_3^-, or changes in NO_3^-/K^+ and NO_3^-/Ba ratios during and after firework events, would help support the proposed mechanism. The conclusion that nitrate formation is a key aging pathway should be stated more cautiously unless primary nitrate contributions can be excluded or quantified.

We thank the reviewer for this critical and constructive comment. We fully agree that nitrate-based oxidizers such as KNO_3 and $Ba(NO_3)_2$ are commonly used in fireworks and may directly emit primary nitrate-containing particles during combustion, and that our original interpretation of nitrate enrichment as solely evidence of atmospheric aging was oversimplified. We acknowledge that our current dataset does not allow us to quantitatively separate primary nitrate emissions from secondary nitrate formation.

To address this, we have re-examined our data and made the following revisions. The temporal relationships among K^+, Ba, Cl^-, and NO_3^- are already presented in Fig. 1 (time series of Ba mass concentration) and Fig. S4 (time series of K^+, Cl^-, and NO_3^- mass concentrations), which capture the synchronous enhancements and post-event decays of these species during firework episodes. In addition, we have performed the following analyses:

(1) **Ratio analyses during and after firework events.** To specifically examine the changes in NO_3^-/K^+ and NO_3^-/Ba ratios during and after firework events, we analyzed their diurnal variations at the NSPZ site during Firework Episode I, using nighttime hours (19:00–05:00) to represent the active firework emission period ("during firework events") and daytime hours (06:00–18:00) to represent the post-firework aging period ("after firework events"). The figure has been included in the Supplement (Fig. S11), and the related discussion has been added to Section 2.4 and 3.3.1.

"In this study, nighttime hours (19:00 – 05:00) were defined as the active firework emission period, and daytime hours (06:00–18:00) as the post-firework aging period." has been added to Section 2.4, Please refer to Lines **128–129** of the revised manuscript.

"It should be noted, however, that fireworks contain nitrate-based oxidizers such as KNO_3 and $Ba(NO_3)_2$, which may directly emit primary nitrate-containing particles upon combustion (Conkling and Mocella, 2010; Wang et al., 2007). Therefore, the observed nitrate enrichment in Ba-containing particles cannot be solely attributed to secondary aging processes. Nevertheless, the diurnal variations of NO_3^-/K^+, NO_3^-/Ba, and Cl^-/NO_3^- mass concentration ratios are consistent with the proposed aging pathway (Fig. S11). The NO_3^-/K^+ ratio was consistently higher during daytime than during nighttime, consistent with greater relative nitrate abundance. Conversely, the

Cl^-/NO_3^- ratio was significantly elevated during nighttime, reflecting the direct emission of chloride-rich particles from active fireworks. In contrast, the NO_3^-/Ba ratio remained relatively stable throughout the diurnal cycle, consistent with the relatively stable ratios observed in Ba-N particles (Fig. 5b). These patterns, together with the temporal lags between OClN and N particle peaks and between gaseous NO_2 and particulate NO_3^-, suggest that secondary nitrate formation via chloride-to-nitrate conversion is an important aging pathway, although primary nitrate emissions from fireworks may also contribute. In our dataset, we cannot fully quantify the relative contributions of these two sources. Future studies using high-time-resolution tracer analyses are needed to better distinguish them." has been added to Section 3.3.1, Please refer to Lines **263**–**274** of the revised manuscript.

The revised Figure S11 and its caption are as follows:

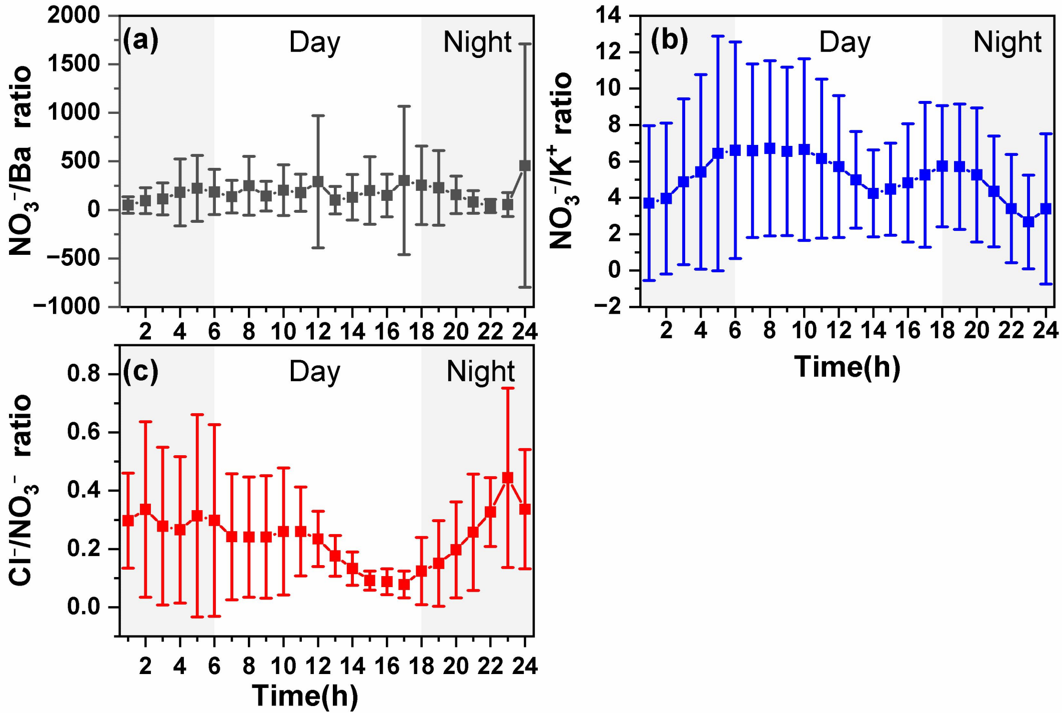

Figure S11. Diurnal variations of NO_3^-/Ba, NO_3^-/K^+ and Cl^-/NO_3^- mass concentration ratios at the NSPZ site during FI.

(2) Cautious conclusion on nitrate formation. We agree that the conclusion on nitrate formation should be stated more cautiously unless primary nitrate contributions can be excluded or quantified. We have therefore revised the relevant parts of the manuscript as follows:

1) Abstract: We revised the statement from "point to nitrate formation as a key aging pathway" to "suggested secondary nitrate formation, although primary nitrate emissions from fireworks could not be excluded.". Please refer to Lines **25–26** of the revised manuscript.

2) Section 3.3.1 (discussion on the limitations): We added a discussion on the limitations, acknowledging that the fireworks contain nitrate-based oxidizers that may directly emit primary nitrate-containing particles, that we cannot fully quantify the relative contributions of primary nitrate emissions versus secondary nitrate formation in our current dataset, and that future studies using high-time-resolution tracer analyses are needed to better distinguish them.

"These patterns, together with the temporal lags between OClN and N particle peaks and between gaseous NO_2 and particulate NO_3^-, suggest that secondary nitrate formation via chloride-to-nitrate conversion is an important aging pathway, although primary nitrate emissions from fireworks may also contribute. In our dataset, we cannot fully quantify the relative contributions of these two sources. Future studies using high-time-resolution tracer analyses are needed to better distinguish them." has been added to the revised manuscript. Please refer to Lines **270–274** of the revised manuscript.

3) **Section 4 (Conclusions):** We have revised the related discussion on nitrate formation in the conclusions section to acknowledge that primary nitrate emissions may also contribute to the observed patterns.

"Primary nitrate emissions and site-specific emission and transport conditions may also have contributed to the observed patterns;" has been added to the revised manuscript. Please refer to Lines **330–331** of the revised manuscript.

We have also added a statement on future research directions: "Future studies should combine near-source sampling with high-time-resolution tracer measurements to distinguish primary nitrate emissions from secondary nitrate formation." Please refer to Lines **343–345** of the revised manuscript.

2. The manuscript identifies OClN particles as relatively fresh emissions and N particles as aged products. However, OClN particles already contain nitrate, and fresh primary firework emissions were not directly sampled. Therefore, OClN should be

described as an “early-aged” or “less aged” state rather than a fresh emission type unless source samples or near-source measurements are available. Additional evidence, such as the temporal evolution of OClN/N ratios after known firework periods, site-to-site aging gradients, wind-direction analysis, or trajectory support, would strengthen this interpretation.

We thank the reviewer for this thoughtful comment. We agree that OClN particles already contain nitrate and thus cannot be considered truly fresh primary emissions, especially since we did not conduct near-source sampling. The term "fresh" was indeed imprecise.

To address this concern, we have revised the terminology throughout the manuscript to describe OClN as "**early-aged**" and N as "**more aged**". Specifically, we have modified the section title "Evidence for fresh and aged particle types..." to "Evidence for early-aged and more aged particle types...", revised the description of OClN from "fresher" to "early-aged" in Section 3.2.2, and updated the Figure 3 caption accordingly.

Following the reviewer's suggestions for additional evidence, we have examined the following:

(1) **Site-to-site aging gradients.** We compared OClN/N particle number ratios across the four sites during the same firework episode (Fig. S7). The highest ratios were observed at NSPZ, particularly during nighttime, consistent with its proximity to active firework zones. At GYQ and CHLK, the ratios were lower, suggesting progressive aging during atmospheric transport.

(2) **Temporal evolution of OClN/N ratios.** We analyzed the diurnal variations of OClN/N ratios at the NSPZ site during Firework Episode I, using nighttime hours (19:00–05:00) to represent the active firework emission period and daytime hours (06:00–18:00) to represent the post-firework aging period. The ratio decreased from nighttime to the following daytime, consistent with the progressive conversion of OClN to N during atmospheric aging.

(3) **Wind-direction analysis.** Wind-direction analysis further supported these site-specific patterns. At PYDXC, higher OClN/N ratios were observed when surface winds came from the direction of the restricted firework zones in Panyu. At NSPZ, higher OClN/N ratios were predominantly associated with winds from the north and

northwest, consistent with its geographical setting (Fig. S8).

(4) **Backward trajectory analysis.** Backward trajectory analysis showed that OClN/N high values at all four sites were predominantly associated with short-range air masses, suggesting local or nearby sources rather than long-range transport (Fig. S9). The methodological description of the CWT analysis has been added to the Supplement.

In addition, we have added a discussion of the limitations at the end of Section 3.2.2, acknowledging that the classification is based on observed chemical evolution in ambient aerosols rather than direct near-source sampling, and that without such reference measurements we cannot definitively characterize the initial emission state of Ba-containing particles.

"To further examine the spatial evolution of the aging process, we compared the OClN/N particle number ratios across the four sites during FI (Fig. S7a). The highest mean OClN/N ratios were observed at NSPZ (Fig. S7a), particularly during nighttime hours (Fig. S7b), consistent with its proximity to active firework emission zones. At GYQ and CHLK, the OClN/N ratios were lower than at NSPZ, suggesting progressive aging of Ba-containing particles during atmospheric transport. Notably, PYDXC, despite being a restricted-firework zone with a moderate Ba-containing particle fraction (2.2%, Table 1) and the highest NO_2 enhancements among all sites (Table 2), exhibited unexpectedly low OClN/N ratios. This may reflect rapid aging driven by locally elevated NO_2 levels, which could accelerate chloride-to-nitrate conversion, or differences in firework composition and local chemical conditions compared to NSPZ. These site-specific patterns, together with the diurnal variations of OClN/N ratios at NSPZ (Fig. S7b), provide complementary evidence for the proposed aging pathway and highlight the role of local chemical environments in modulating the aging process. Wind-direction analysis also supported these site-specific patterns, with higher OClN/N ratios at PYDXC corresponding to the direction of restricted firework zones, and at NSPZ predominantly from the north and northwest, consistent with its geographical setting (Fig. S8). Backward trajectory analysis further showed that, at all four sites, OClN/N high values were predominantly associated with short-range air masses, suggesting local or nearby sources rather than long-range transport (Fig. S9)." has been added to Section 3.2.2. Please refer to Lines **220–233** of the revised manuscript.

"It should be acknowledged that the classification of OClN and N particles as early-aged and more aged states is based on observed chemical evolution in ambient aerosols, rather than on direct near-source sampling of fresh firework emissions. Without such reference measurements, we cannot definitively characterize the initial emission state of Ba-containing particles. Nevertheless, the consistent temporal patterns support the interpretation that OClN particles represent a less advanced stage of aging compared to N particles." has been added to Section 3.2.2. Please refer to Lines **234–238** of the revised manuscript.

The revised Figures S7–S9 are as follows:

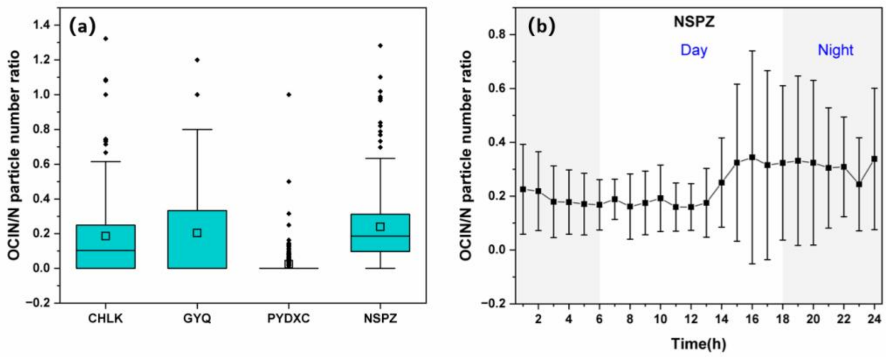

Figure S7. OClN/N particle number ratios during FI. (a) OClN/N ratios at the four sites; (b) Diurnal variations of OClN/N ratios at the NSPZ site.

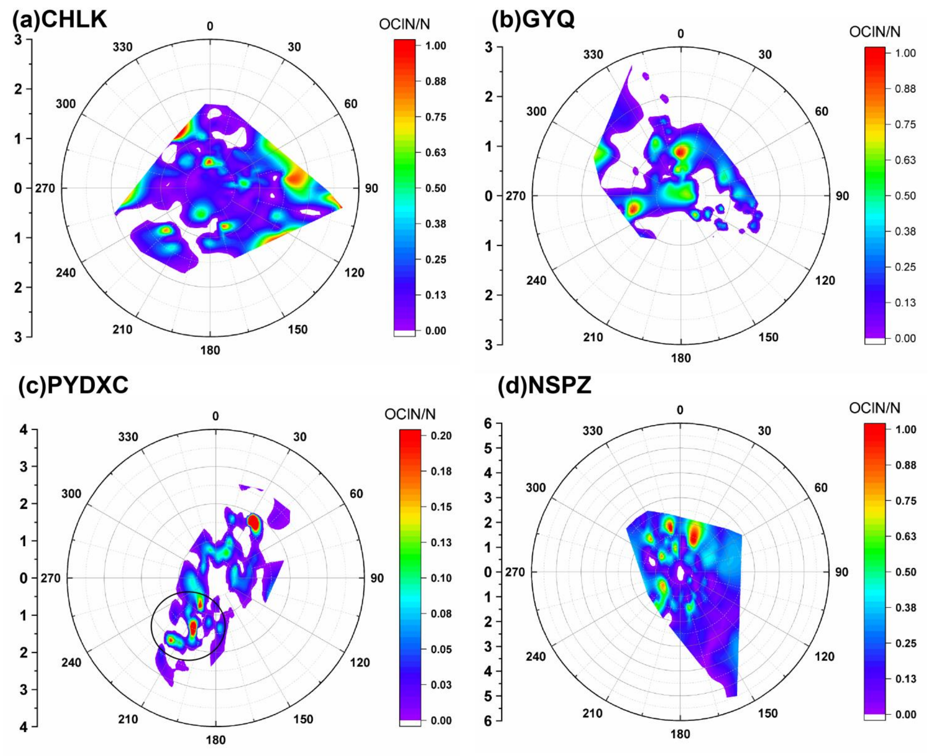

Figure S8. Wind-direction dependence of OClN/N particle number ratios at the four sites during FI. Colors indicate OClN/N ratio values (see legend). Higher OClN/N ratios indicate a larger proportion of early-aged OClN particles. The dashed circle in panel (c) highlights the direction corresponding to the Shiqi Town area, a designated restricted firework zone in Panyu.

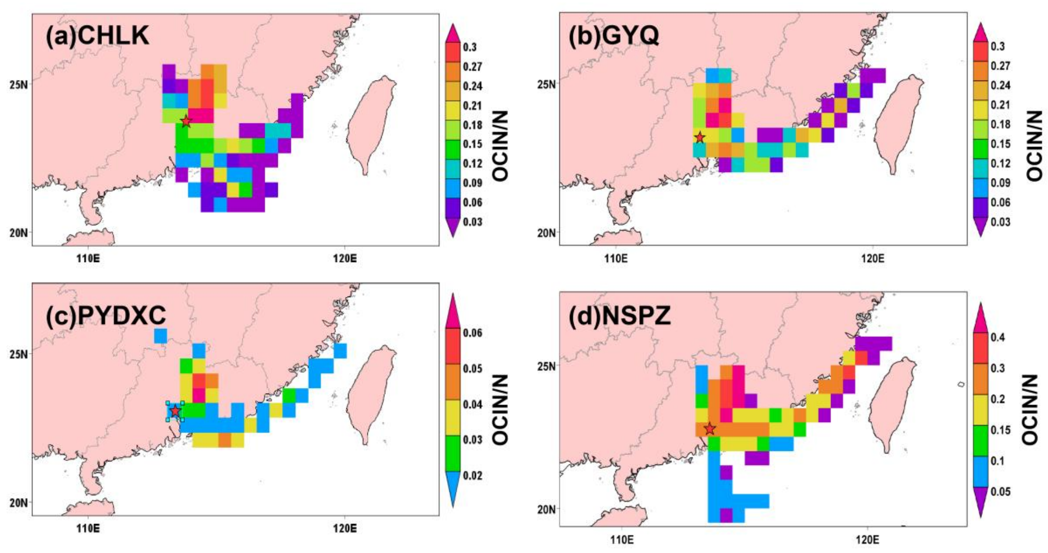

Figure S9. CWT plots of potential source areas of OClN/N particle number ratios at the four sites during FI, respectively. Trajectories were calculated using HYSPLIT4 and visualized with MeteoInfo. © OpenStreetMap contributors.

3.The policy effectiveness conclusion is somewhat overstated. The higher Ba concentrations in restricted zones than in the urban prohibited zone are consistent with a policy effect, but they do not quantitatively demonstrate policy effectiveness. Site differences may also reflect local firework activity, enforcement intensity, meteorology, population behavior, transport, and distance to emission hotspots. The authors should revise this conclusion more cautiously. A stronger policy claim would require additional evidence such as enforcement records, observed firework activity, wind fields, or comparisons with pre-policy periods.

We thank the reviewer for the critical and constructive comments.We agree that the original wording overstated the certainty of the policy-related conclusion. To better evaluate the influence of atmospheric transport, we have added wind-direction analysis and backward-trajectory analysis (Fig. S8–S9). The wind-direction analysis shows that higher OClN/N ratios at PYDXC were associated with air masses from the direction of the restricted firework zones, while at NSPZ they were predominantly from the north and northwest, consistent with its geographical setting. The backward-trajectory analysis further shows that high OClN/N values at all four sites were predominantly associated with short-range air masses, indicating that local or nearby sources, rather than long-range transport, were the main contributors to the observed site-to-site differences.

The concentration data show that GYQ (prohibited zone) had a lower peak Ba concentration than PYDXC (restricted zone), despite the much higher population density of GYQ. This contrast is consistent with a potential mitigating role of stricter controls, but does not quantitatively establish causality. Concentrations at NSPZ were slightly lower than at GYQ, indicating that regulatory status alone did not determine the full spatial pattern. Other factors, such as local firework activity, enforcement, meteorology, transport, and proximity to sources, may also have contributed.

We have therefore removed claims that the pattern was "governed by" policy or that policy "can override population density as the dominant factor." The revised manuscript now presents the interpretation as preliminary observational evidence, while acknowledging that the independent policy contribution cannot be quantified from the current data. The abstract has been revised accordingly.

The additional figures S8, S9 and the related discussions:

"Wind-direction analysis also supported these site-specific patterns, with higher

OClN/N ratios at PYDXC corresponding to the direction of restricted firework zones, and at NSPZ predominantly from the north and northwest, consistent with its geographical setting (Fig. S8). Backward trajectory analysis further showed that, at all four sites, OClN/N high values were predominantly associated with short-range air masses, suggesting local or nearby sources rather than long-range transport (Fig. S9)." Please refer to Lines **229–233** of the revised manuscript.

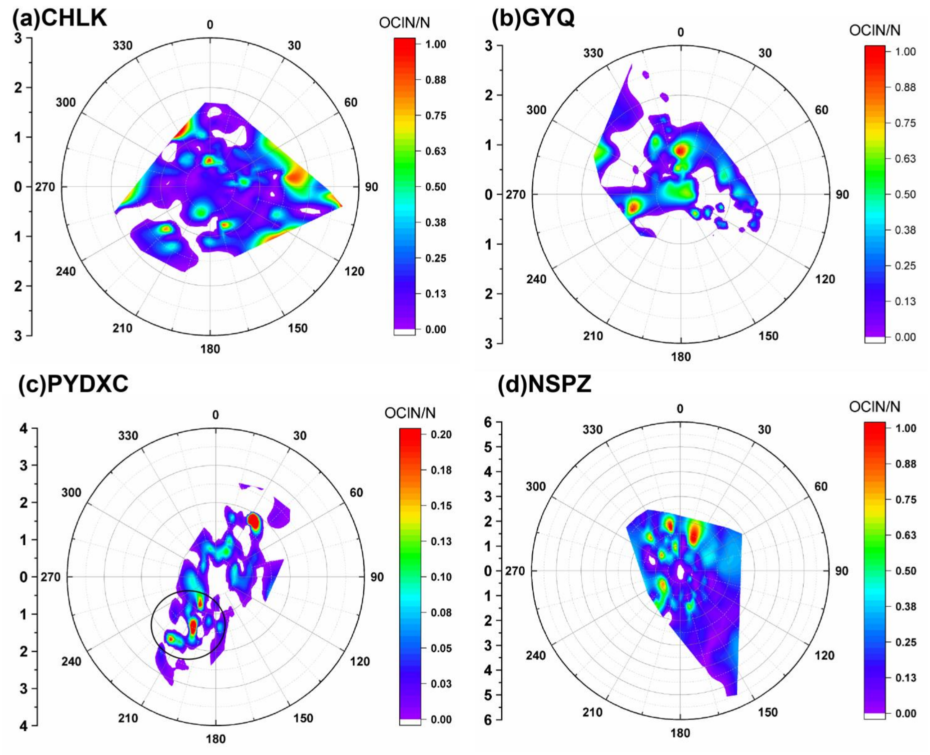

Figure S8. Wind-direction dependence of OClN/N particle number ratios at the four sites during FI. Colors indicate OClN/N ratio values (see legend). Higher OClN/N ratios indicate a larger proportion of early-aged OClN particles. The dashed circle in panel (c) highlights the direction corresponding to the Shiqi Town area, a designated restricted firework zone in Panyu.

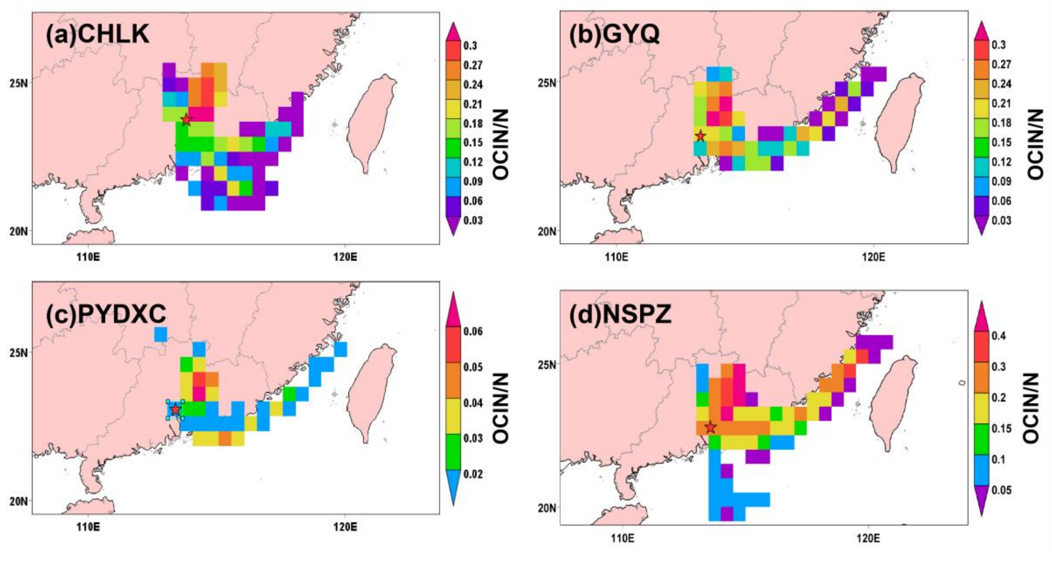

Figure S9. CWT plots of potential source areas of OClN/N particle number ratios at the four sites during FI, respectively. Trajectories were calculated using HYSPLIT4 and visualized with MeteoInfo. © OpenStreetMap contributors.

The revised sentence in the Section 3.1.2:

"The observed urban–rural gradient appears to be associated with regulatory measures and human activity intensity rather than simple downwind dispersion, and both $PM_{2.5}$ and Ba peak mass concentrations exhibited similar spatial patterns (Fig. 2). The highest concentration ($PM_{2.5}$: 89 μg m^{-3}; Ba: 3,411 ng m^{-3}) occurred at PYDXC, a restricted-fireworks suburban area with high population density (5,327 people km^{-2}; Guangzhou Statistical Yearbook, 2023). In contrast, the urban core site (GYQ), despite higher population density (28,400 people km^{-2}, 2023 data), exhibited lower peak concentrations. Concentrations at suburban NSPZ were slightly lower than the urban core, while the rural background site (CHLK) showed the lowest levels. This pattern suggests that regulatory policy (ban vs. restriction) is consistent with a possible influence on spatial heterogeneity of peak pollution during episodic events, although other factors such as local firework activity, enforcement intensity, meteorological conditions, atmospheric transport, and proximity to emission sources may also contribute (Kong et al., 2015). Thus, our interpretation should be considered preliminary and warrants verification with additional data (e.g., enforcement records and wind field analysis)." has been added to the revised manuscript. Please refer to Lines **174–184** of the revised manuscript.

The revised sentence in the abstract:

"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. The health risk assessment is too simplified for the conclusions drawn. The use of an oral reference dose as a substitute for inhalation exposure and the reliance on average concentrations provide only a preliminary screening-level estimate. Firework exposure is highly episodic, and short-term peaks may be more relevant than long-term average HQ values, especially for children and individuals with respiratory or cardiovascular conditions. The authors should clearly present this analysis as preliminary, justify the use of oral RfD for inhalation more carefully, and discuss uncertainties related to Ba chemical speciation, solubility, and bioavailability.

We thank the reviewer for this critical and constructive comment. We agree that the health risk assessment was oversimplified. As the primary focus of this study is on the atmospheric aging mechanisms of firework-derived Ba-containing particles, the health risk analysis was intended as a supplementary context rather than a core conclusion.

To address this, we have revised the manuscript by: (1) explicitly presenting the analysis as preliminary and screening-level, including changing the titles of Section 2.5 and Section 3.4 to "Preliminary exposure and risk assessment methodology" and "Preliminary exposure and risk assessment," respectively; (2) clarifying that the oral RfD was used as a surrogate in the absence of an established inhalation RfC for Ba; (3) adding a discussion on the episodic nature of firework exposure and the observed short-term peak concentrations in Section 3.4; and (4) expanding the uncertainty discussion in Section 3.4 to include Ba chemical speciation, solubility, and bioavailability. (5) revising the health-related statements in the abstract and conclusions to reflect the screening-level nature of this analysis. Detailed revisions are as follows.

The specific revisions are as follows:

(1) **Preliminary nature:** The titles of Section 2.5 and Section 3.4 have been changed to "Preliminary exposure and risk assessment methodology" and "Preliminary exposure and risk assessment," respectively. We have explicitly described the analysis as a screening-level estimate throughout both sections.

(2) **RfD justification:** In Section 2.5, we have added a clear statement that in the absence of an established inhalation reference concentration (RfC) for Ba, the oral RfD is used a surrogate. We acknowledge that this substitution may introduce

uncertainty regarding inhalation-specific bioavailability.

The revised content is as follows: "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." Please refer to Lines **132–134** of the revised manuscript.

(3) **Episodic exposure and short-term peaks:** In Section 3.4, we have added a discussion highlighting that Ba concentrations exhibit sharp spikes lasting only a few hours during active firework periods (Fig. 1a), with short-term peak concentrations 1–3 orders of magnitude above background levels. We also note that a formal acute HQ was not calculated due to the lack of an established acute inhalation reference value for Ba, and that these transient exposure events may pose a greater concern than the long-term average would indicate, particularly for children and individuals with pre-existing respiratory or cardiovascular conditions.

The revised content is as follows: "Firework exposure is highly episodic, with Ba mass concentrations exhibiting sharp spikes lasting only a few hours during active firework periods (Fig. 1a). While the chronic HQ based on long-term average concentrations was below 1, the short-term peak concentrations during these episodes were 1–3 orders of magnitude higher than background levels. A formal acute HQ was not calculated due to the lack of an established acute reference value for Ba. Nevertheless, the elevated peak concentrations suggest that transient exposure events may pose a greater concern than the long-term average would indicate, particularly for children and individuals with pre-existing respiratory or cardiovascular conditions." Please refer to Lines **312–317** of the revised manuscript.

(4) **Uncertainties:** We have expanded the uncertainty discussion to explicitly address three aspects: (a) the use of oral RfD as a substitute for inhalation risk assessment may not fully capture inhalation-specific bioavailability; (b) the health risk may depend on Ba chemical speciation (e.g., $BaCl_2$ vs. $Ba(NO_3)_2$), solubility, and bioavailability, which were not directly measured in this study (ATSDR, 2021); and (c) these factors represent important uncertainties in this preliminary screening-level

assessment and warrant further investigation.

The revised content is as follows: "Several uncertainties should be considered in interpreting these results. First, the use of an oral RfD as a substitute for an inhalation reference concentration may not fully capture inhalation-specific bioavailability. Second, the health risk of Ba-containing particles may depend on their chemical speciation (e.g., $BaCl_2$ vs. $Ba(NO_3)_2$), solubility, and bioavailability, which were not directly measured in this study (ATSDR, 2021). These factors represent important uncertainties in this preliminary screening-level assessment and warrant further investigation. However, this interpretation is qualitative and does not imply a quantified acute health risk, as no formal acute HQ was calculated." Please refer to Lines **318–323** of the revised manuscript.

(5) **Abstract and Conclusions:** We have revised the health-related statements in the abstract and conclusions to reflect the screening-level nature of this analysis.

The Abstract now reads: "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.

In the Conclusions, the statement 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." Please refer to Lines **338–341** of the revised manuscript.

5. The manuscript should define all abbreviations when first used, including OClN, N, NS, S, HMOC, and RPA.

We thank the reviewer for this comment. We have carefully checked the manuscript and added definitions for all abbreviations at their first occurrence, including OClN (rich in oxygen, chloride, and nitrate), N (nitrate-dominated), NS (nitrate and sulfate internally mixed), and S (sulfate-dominated), HMOC (high-molecular-weight organic matter), and RPA (relative peak area).

"The relative peak area (RPA), defined as the fractional peak area of each *m/z* peak relative to the sum of peak areas in the mass spectrum (Healy et al., 2013; Lian et al., 2021), was used to quantify the relative abundance of chemical species in a particle." has been added to the revised manuscript. Please refer to Lines **118–120** of the revised manuscript.

Healy, R. M., Sciare, J., Poulain, L., Crippa, M., Wiedensohler, A., Prevôt, A. S. H., Baltensperger, U., Sarda-Estevè, R., McGuire, M. L., Jeong, C. H., McGillicuddy, E., O'Connor, I. P., Sodeau, J. R., Evans, G. J., and Wenger, J. C.: Quantitative determination of carbonaceous particle mixing state in Paris using single-particle mass spectrometer and aerosol mass spectrometer measurements. Atmos. Chem. Phys. 13 (18), 9479−9496, https://doi.org/10.5194/acp-13-9479-2013, 2013.

Lian, X., Zhang, G., Yang, Y., Lin, Q., Fu, Y., Jiang, F., Peng, L., Hu, X., Chen, D., Wang, X., Peng, P.A., Sheng, G., and Bi, X.H.: Evidence for the formation of imidazole from carbonyls and reduced nitrogen species at the individual particle level in the ambient atmosphere. Environ. Sci. Technol. Lett. 8, 9–15, https://doi.org/10.1021/acs.estlett.0c00722, 2021.

6. The health risk section should avoid the heading "Health effects of Ba from fireworks" because the study does not directly measure health effects. A better heading would be something like "Preliminary exposure and risk assessment."

We thank the reviewer for this suggestion. We agree that the original heading "Health effects of Ba from fireworks" was inappropriate, as our study did not directly measure health effects. We have revised the heading to "Preliminary exposure and risk assessment" to more accurately reflect the scope of our analysis.

7. The manuscript should be carefully edited for grammar, formatting, and consistency, including spacing around units, use of subscripts/superscripts, and consistency in the terms "firework" and "fireworks."

We thank the reviewer for this comment. We have carefully edited the manuscript and Supplement for grammar, spacing, units, subscripts and superscripts, figure labels, and terminology. We standardized the context-dependent use of "firework" as an attributive modifier (e.g., firework emissions, firework events) and "fireworks" as a noun. Representative corrections include consistent formatting of $PM_{2.5}$, NO_3^-, SO_4^{2-}, and units throughout the text and figures.