Response to Reviewers

Thanks for the reviewers' insightful comments on our manuscript entitled "*Measurement report: Insights into seasonal dynamics and planetary boundary layer influences on aerosol chemical components in suburban Nanjing from a year-long observation*". We greatly appreciate the valuable feedback, which has been instrumental in improving the quality of our work. All comments have been carefully considered and addressed. In accordance with the instructions provided in your letter, we have updated the revised manuscript accordingly. Our responses are highlighted in blue, and changes made to the manuscript are marked in red for ease of reference. Please note that the line numbers referenced in our response correspond to those in the original manuscript submission, not the revised version with tracked changes.

Response to RC1

This manuscript presents a comprehensive 1-year dataset on the seasonal dynamics of $PM_{2.5}$ chemical components in suburban Nanjing, with particular emphasis on the role of planetary boundary layer height (PBLH). The study is well-structured, and the results provide valuable insights into aerosol–PBL interactions in the Yangtze River Delta. Overall, the paper is suitable for publication after addressing the following comments.

Major Comments

Major Comments 1. Sensitivity of nitrate to PBLH: One of the central conclusions is that nitrate is the most sensitive component to PBLH changes (Section 3.4), supported by the sharp concentration increase under low-PBLH conditions. However, the mechanism remains unclear. It is not evident whether this increase is primarily driven by suppressed thermodynamic volatilization, enhanced chemical production (e.g., N_2O_5 hydrolysis), or both. The authors are encouraged to analyze the joint distribution of nitrate concentration with temperature and relative humidity across different PBLH intervals. Such an analysis would clarify the dominant drivers of nitrate buildup under low PBLH and strengthen the mechanistic interpretation beyond statistical correlations.

Response: We thank the reviewer for the insightful comments. We fully agree that clarifying the response mechanism of nitrate to PBLH changes is essential. Following the suggestion, we have conducted a more in-depth analysis by integrating further literature review with our observational data, added Figure S7 in the supplement, and have revised the manuscript accordingly.

During winter, T across all PBLH intervals remained similarly low (around 6°C) (Fig. 8d2), indicating that T alone was not the key variable driving the rapid nitrate increase under low PBLH—all intervals provided the low- T conditions required for the thermodynamic stability of ammonium nitrate (Kang et al., 2022).

Instead, humidity played the dominant role. RH showed a significant negative correlation with PBLH: lower PBLH was associated with higher RH (Fig. S7). High RH is a key factor driving nitrate formation through heterogeneous reactions such as N_2O_5 hydrolysis (Peng et al., 2024). When PBLH dropped to 300–500 m, RH reached 84.4%, creating a highly efficient environment for N_2O_5 hydrolysis and leading to rapid chemical nitrate production.

In addition, low PBLH confined gaseous precursors such as NO_X and HNO_3 within the shallow surface layer, increasing their concentrations. The accumulation of precursors, combined with high RH, resulted in a strong synergistic effect that further promoted nitrate formation.

It is also important to emphasize that the consistently low *T* provided a thermodynamic foundation for nitrate stability, preventing significant volatilization of particulate ammonium nitrate and thereby supporting the chemical accumulation process.

In summary, the high sensitivity of nitrate to PBLH in winter primarily stems from the high relative humidity under low PBLH conditions, which strongly promotes heterogeneous chemical production, while the prevailing low temperatures provide the necessary thermodynamic background for nitrate stability.

We have incorporated the above mechanism analysis into the relevant sections of the paper. We thank the reviewer again for helping to enhance the scientific depth of our work.

In 3.4 Sensitivity of $PM_{2.5}$ chemical components to PBLH

In winter, all aerosol chemical components exhibit heightened sensitivity to PBLH. As PBLH decreases, both the rise in mass concentration and the S_{PBLH} are significantly greater than in other seasons (Fig. 8d2, d3). Nitrate shows the greatest sensitivity to PBLH, with its S_{PBLH} reaching a peak value exceeding 2. Within the 300–500 m PBLH range, nitrate constitutes 25.0% of $PM_{2.5}$, emerging as the dominant component (Fig. 8d1).The consistently low *T* (~6°C) across all PBLH intervals (Fig. 8d2) fosters conditions conducive to thermodynamic stability of ammonium nitrate (Kang et al., 2022). As illustrated in Fig. S8d, low PBLH conditions are associated with elevated RH and reduced WS. This humid environment markedly enhances nitrate formation through heterogeneous pathways, such as N_2O_5 hydrolysis (Peng et al., 2024). Simultaneously, low PBLH limits the vertical diffusion of precursors, leading to their accumulation near the surface and further boosting chemical production efficiency. The pronounced sensitivity of nitrate highlights the critical need for proactive emission control measures to avert the swift escalation of severe pollution episodes in winter.

……Nitrate exhibits the highest sensitivity to PBLH across all seasons, with particularly pronounced effects under low PBLH conditions in winter. Its rapid accumulation during this period is primarily fueled by the high humidity linked to low PBLH, which vigorously promotes heterogeneous reactions like N_2O_5 hydrolysis. At the same time, the sustained low temperatures ensure the thermodynamic stability required for nitrate to persist in the particulate phase.

In Supplement

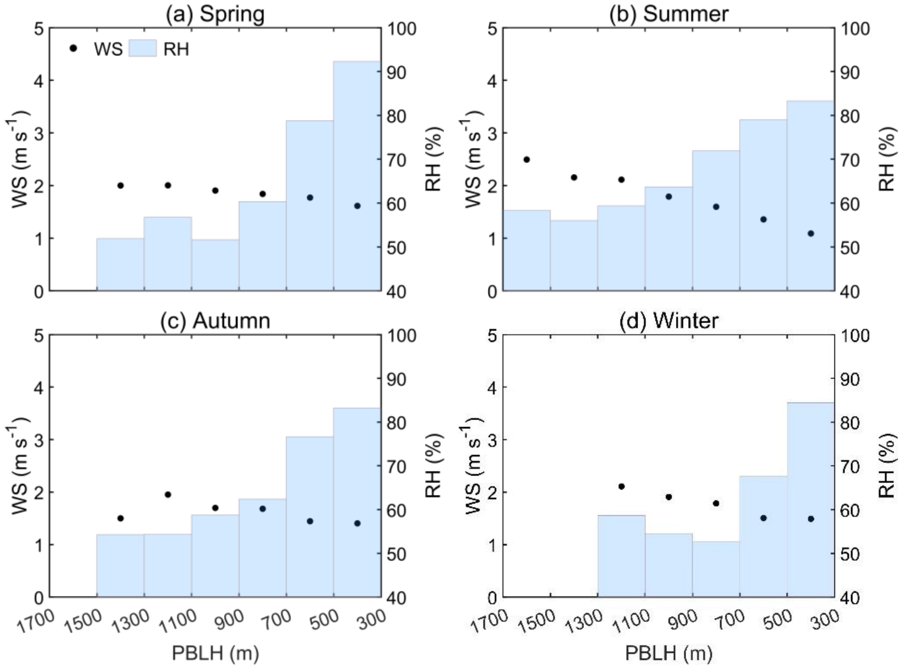

Figure S7: Variations in WS (left y-axis, black dots) and RH (right y-axis, blue columns) as a function of planetary boundary layer height (PBLH) across four seasons. Data are grouped into PBLH bins with 200 m increments, excluding bins with fewer than 10 data points.

Major Comments 2. Conceptual figure: Consider adding a schematic (conceptual diagram) to synthesize the key findings. A figure linking seasonal variations, PBLH effects, and dominant aerosol components would improve accessibility and provide readers with an integrated overview.

Response: We agree that a conceptual synthesis will greatly enhance the manuscript. Accordingly, we have created a new schematic diagram that integrates the key findings on seasonal variations, PBLH influences, and the dominant aerosol components. Figure 11 in the manuscript provides an intuitive overview of the study's main conclusions, and we believe it significantly improves the accessibility and impact of the work.

In 4 Summary and conclusions

PBLH differentially modulates $PM_{2.5}$ chemical components, with underlying mechanisms depicted in Fig.11. High PBLH facilitates the dispersion of primary aerosols and nitrate, significantly reducing their mass concentrations, especially during daytime in warmer seasons. However, SOA and sulfate accumulation persist under high PBLH due to robust photochemical formation, and thus they are less sensitive to PBLH variations. In a cold and humid winter, low PBLH facilitates nitrate formation and accumulation, which in turn further inhibits the development of PBL, establishing a positive feedback loop that leads to an explosive growth in nitrate concentrations.

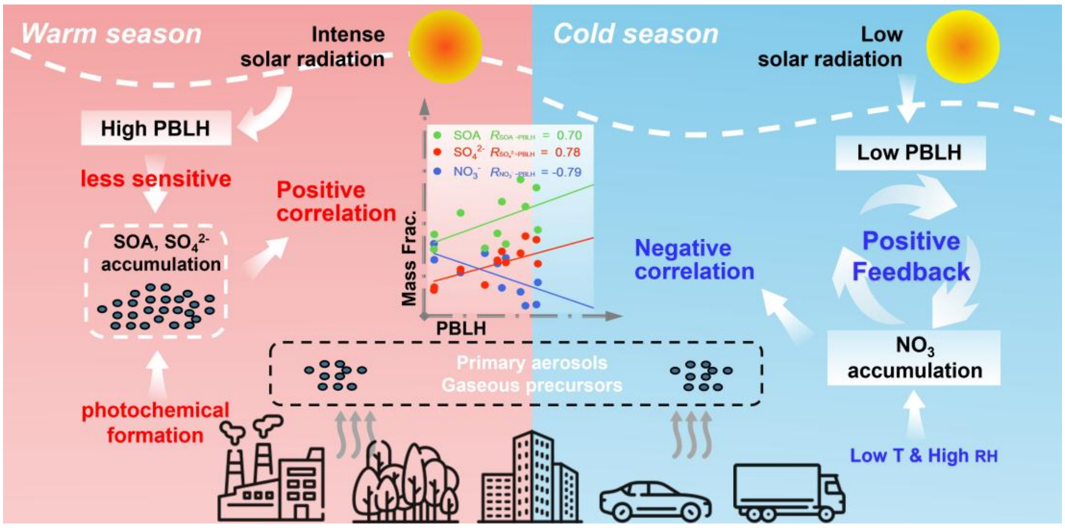

Figure 11: Schematic diagram illustrating seasonal contrasts in the relationships between PBLH and $PM_{2.5}$ chemical components. During the warm season, intense photochemical oxidation under elevated PBLH enhances the formation of SOA and sulfate, both of which exhibit relatively low sensitivity to PBLH variations. In contrast, the cold season features lower PBLH, which facilitates nitrate formation and accumulation, reinforced by a strong positive feedback loop between heightened aerosol loading and boundary layer suppression.

Major Comments 3. Regional transport vs. local formation: The PSCF and pollution rose analyses provide strong evidence of seasonal source regions. However, the discussion could better disentangle the relative roles of regional transport and local photochemical/heterogeneous formation under different PBLH regimes. For example, the paper notes sulfate's regional transport characteristics but does not explicitly compare this with in-situ secondary formation under varying boundary layer conditions. Expanding this discussion would clarify how transport and local chemistry interact.

Response: We thank the reviewer for this insightful suggestion regarding the need to better disentangle the roles of regional transport and local formation under different PBLH regimes. We have thoroughly revised the discussion in Section 3.5 to address this comment by systematically integrating PBLH data from pollution roses with our source analysis. The key improvement lies in explicitly linking PBLH conditions to the dominant formation pathways for each component.

In 3.5 Source apportionment of $PM_{2.5}$ chemical components

PSCF analysis and pollution rose diagrams (Fig. 9 and 10) reveal distinct seasonal source patterns for $PM_{2.5}$ chemical components. For POA, high-potential source areas are predominantly located south of the NUIST site during spring, summer, and autumn (Fig. 9a), with elevated concentrations in the pollution roses occurring mainly at low wind speeds from southeasterly directions (Fig. 10a). This pattern suggests dominant influences from local industrial emissions. In winter, however, POA source regions expand northward to the NCP (Fig. 9a4), and the pollution roses indicate high POA concentrations at higher WS from northerly and southeasterly directions (Fig. 10a4), pointing to a combination of local emissions and long-range transport from the north (Cao et al., 2022). POA concentrations generally exhibit an inverse relationship with PBLH in the pollution roses (Fig. 10a1-

a4 vs. e1-e4), highlighting the role of a lower PBLH in promoting primary aerosol accumulation. Notably, in winter, under northeasterly winds of 4–4.5 m s^{-1}, all components show peak concentrations, corresponding to a PBLH of ~570 m (Fig. 10a4-e4). Although this PBLH is not the seasonal minimum, it facilitates horizontal transport of industrial and urban pollutants from the northeast while suppressing vertical dispersion, collectively leading to heavy pollution.

Similar PSCF and pollution rose patterns for POA and SOA in summer (Figs. 9a2, b2, and 10a2, b2) imply shared emission sources, corroborating enhanced photochemical activity that drives rapid SOA formation from gaseous precursors and POA conversion under elevated temperatures. SOA's high-potential sources in summer and autumn concentrate in southeastern forested hills south of the site (Figs. 9b2 and b3), aligning with concentration maxima under southeasterly winds (Figs. 10b2 and b3). Elevated SOA under easterly winds and higher wind speeds corresponds to increased PBLH, facilitating precursor transport. This aligns with southeastern monsoon flows conveying biogenic precursors from southern forests (Wang et al., 2017). Summer SOA peaks at lower wind speeds suggest local formation alongside regional transport, whereas autumn patterns emphasize stronger transport. In winter, SOA sources expand to the NCP (Fig. 9b4), with peaks under northerly winds (Fig. 10b4). Associated higher PBLH indicates substantial long-range northern transport contributions to winter SOA.

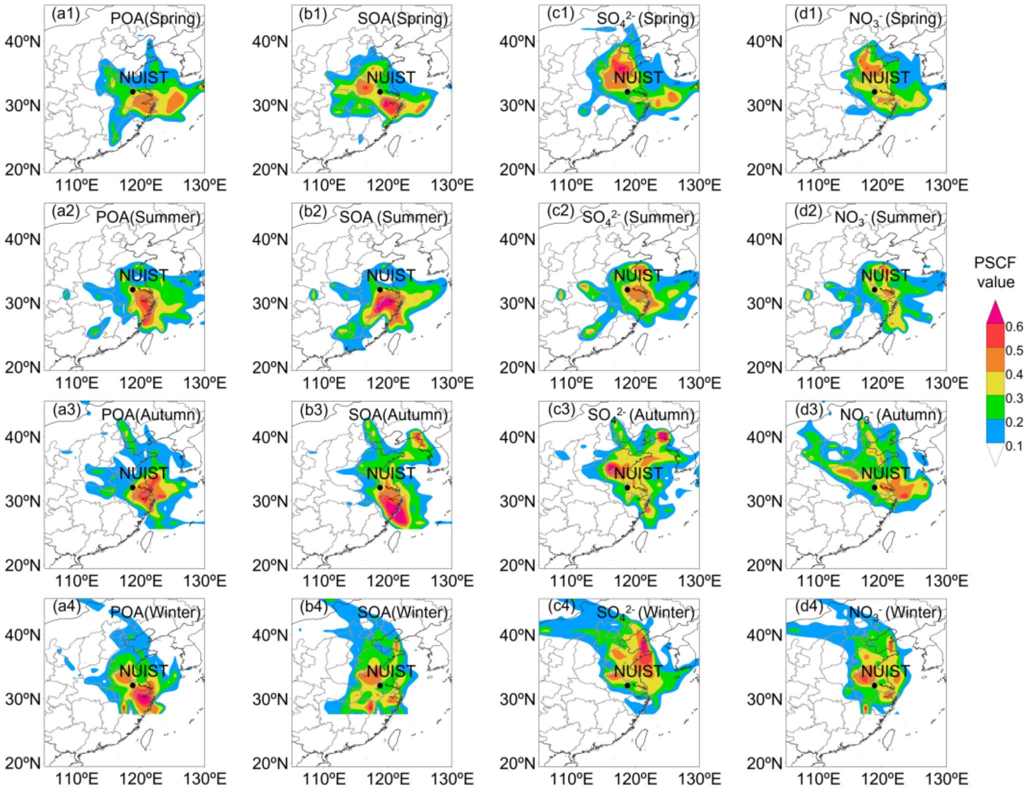

Figure 1: PSCF analysis of (a) POA, (b) SOA, (c) sulfate, and (d) nitrate in PM$_{2.5}$ during four seasons. The black dot indicates the NUIST site. The color scale indicates the values of PSCF.

Sulfate source regions predominantly localize within the YRD in summer (Fig. 9c2), with concentration maxima at low WS (Fig. 10c2), underscoring the prevalence of local photochemical formation under elevated *T*. In spring, autumn, and winter, these regions shift northward to the NCP (Fig. 9c), exhibiting more dispersed high-concentration patterns in pollution roses (Figs. 10c1, c3 and c4), indicative of enhanced regional transport. This seasonal dichotomy aligns with sulfate's diurnal patterns. Furthermore, elevated sulfate concentrations under higher WS and PBLH across all seasons reinforce the significance of long-range transport.

Nitrate source regions localize proximate to the NUIST site in summer (Fig. 9d2), with concentration maxima at low WS (Fig. 10d2), attributable to nitrate's elevated volatility and constrained transport under warm conditions. In winter, nitrate sources coincide with those of SOA (Fig. 9d4), promoted by low *T* and high RH that enhance aqueous-phase formation. Winter nitrate peaks manifest at higher WS in the pollution rose (Fig. 10d4), inversely correlating with PBLH distribution, thereby emphasizing the shallow boundary layer contribution to nitrate accumulation via inhibited vertical dispersion and expedited chemical production.

These results elucidate the interactions among local emissions, regional transport, and meteorological factors (e.g., WD, PBLH) in determining $PM_{2.5}$ chemical composition. The differentiated source patterns emphasize the imperative for tailored emission control strategies, including reductions in industrial and combustion sources within the YRD and northern provinces to attenuate winter POA and nitrate, as well as regulation of biogenic precursors to curtail summer SOA.

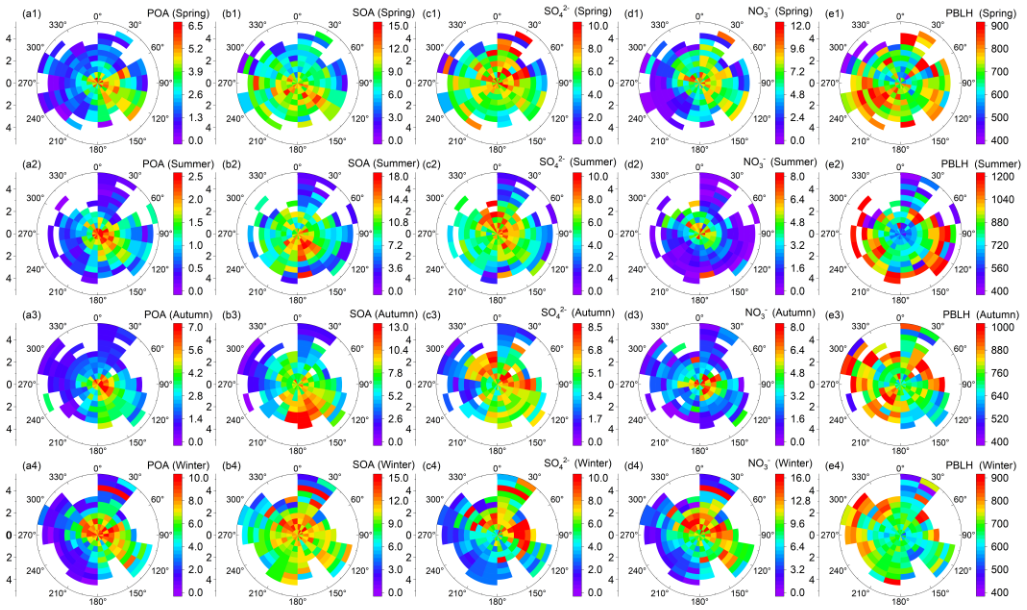

Figure 2: Pollution roses of (a) POA, (b) SOA, (c) sulfate, and (d) nitrate during four seasons. The data are grouped into grids with increments of WS and WD being 0.5 m $s^{-1}$and 20°, respectively. The unit of color scale is μg m^{-3}.

Major Comments 4. Link to air quality management: The policy implications in the conclusions are valuable but could be made more explicit. For instance, the recommendation to reduce NO_x in winter and VOCs in summer could be directly tied to the mechanistic findings (e.g., nitrate sensitivity to PBLH vs. SOA formation under strong photochemistry). Strengthening these connections would enhance the paper's impact for both scientific and regulatory audiences.

Response: We fully agree that explicitly linking the mechanistic findings to policy recommendations enhances the impact of our work. In response, we have revised the manuscript to strengthen these connections.

In 3.3 Diurnal dynamics of $PM_{2.5}$ chemical components

…The persistent bimodal pattern confirms that targeted traffic emission controls during morning and evening rush hours would effectively curtail exposure to primary pollutants like BC and POA in the urban environment.

…It implies that curtailing the key precursor emissions VOCs and SO_2, during the morning and early afternoon in summer could effectively suppress the photochemical formation of SOA and sulfate, thereby alleviating daytime particulate pollution.

…The contrasting diurnal patterns highlight distinct control strategies: broad NO_X reductions in warm seasons, contrasted with stringent NO_X controls during winter mornings and nights to impede rapid nitrate accumulation facilitated by stable conditions.

…These patterns inform time-specific emission control strategies, encompassing traffic controls during rush hours to mitigate primary aerosols, precursor reductions during peak photochemical periods to limit secondary aerosols, and rigorous winter NO_X controls during nights and mornings to avert severe nitrate pollution.

In 3.4 Sensitivity of $PM_{2.5}$ chemical components to PBLH

…The pronounced sensitivity of nitrate highlights the critical need for proactive emission control measures to avert the swift escalation of severe pollution episodes in winter.

Minor Concerns

Minor Concerns 1. The Summary and Conclusions section is slightly lengthy. Please condense it to highlight the most important findings and implications.

Response: We thank the reviewer for this suggestion. We have thoroughly revised the Summary and Conclusions section to make it more concise and focused. The revised version now more directly highlights the core findings. Redundant descriptions and secondary details have been removed to improve readability and impact.

In 4 Summary and conclusions

This study reveals distinct seasonal and diurnal patterns in $PM_{2.5}$ chemical composition and their interactions with meteorological factors, particularly PBLH. $PM_{2.5}$ exhibits pronounced seasonal variations, ranging from 20.4 $\mu g\ m^{-3}$ in July to 48.3 $\mu g\ m^{-3}$ in December. Stable meteorological conditions, characterized by low PBLH (e.g., 673.4 m in winter) and low WS, promote the accumulation of primary aerosols, including POA, BC, and chloride, particularly during winter haze episodes. Secondary aerosols, mainly including SOA, sulfate, and nitrate, show strong *T* dependencies, with SOA and sulfate peaking in summer due to intense photochemical oxidation, while nitrate dominates in winter under low *T* and high RH.

PBLH differentially modulates $PM_{2.5}$ chemical components, with underlying mechanisms depicted in Fig.11. High PBLH facilitates the dispersion of primary aerosols and nitrate, significantly reducing their mass concentrations, especially during daytime in warmer seasons. However, SOA and sulfate accumulation persist under high PBLH due to robust photochemical formation, and thus they are less sensitive to PBLH variations. In a cold and humid winter, low PBLH facilitates nitrate formation and accumulation, which in turn further inhibits the development of PBL, establishing a positive feedback loop that leads to an explosive growth in nitrate concentrations. Diurnal variations further highlight PBLH's role: primary aerosols show bimodal patterns linked to traffic emissions, while SOA and sulfate increase during daytime due to photochemical activity, moderated by PBLH-driven dispersion. POA is influenced by local emissions and long-range transport from the north in winter. SOA sources concentrate in southeastern hilly forest areas in summer and autumn, driven by biogenic precursor transport, while winter SOA aligns with northern coal combustion sources under low PBLH. Sulfate sources localize within the YRD in summer but shift to the NCP in other seasons, reflecting regional transport. Nitrate sources cluster near the NUIST site in summer due to its volatility, but align with northern sources in winter, enhanced by aqueous-phase formation and low PBLH.

These findings underscore the complex interplay of local emissions, regional transport, and meteorological factors in shaping $PM_{2.5}$ pollution in the YRD. The differential responses of $PM_{2.5}$ chemical components to PBLH highlight the need for targeted air quality strategies. Reducing industrial and combustion emissions in the YRD and northern regions can mitigate winter POA and nitrate pollution, while controlling volatile organic compound emissions is critical for reducing summer SOA. Targeted traffic, precursor, and NO_X emissions at critical periods can effectively mitigate both primary and secondary aerosol formation. These insights provide a scientific foundation for developing season-specific air quality management policies in Nanjing and the broader YRD, addressing both local and regional pollution sources to improve public health and environmental quality.

Minor Concerns 2. In Section 2.2, abbreviations (e.g., ACSM, OA, NO_3^-, SO_4^{2-}, NH_4^+, Chl, BC) are somewhat repetitive. Please streamline and ensure consistency throughout the manuscript.

Response: We have thoroughly reviewed the entire manuscript to streamline the use of abbreviations and ensure consistency, following the reviewer's suggestion.

In 2.2 Instruments

A Q-ACSM, equipped with a $PM_{2.5}$ lens system, is used to measure non-refractory $PM_{2.5}$ (NR-$PM_{2.5}$) components, including organic aerosol, nitrate, sulfate, ammonium, and chloride.

Minor Concerns 3. In several figures (e.g., Fig. 2 and Fig. 5), labels and legends are too small. Please enlarge font size or bold key elements to improve readability.

Response: We thank the reviewer for this suggestion. We have carefully reviewed all figures throughout the manuscript and have specifically increased the font sizes of the labels, legends, and key elements in **Figures 2 and 5** to significantly enhance readability.

In 3.1 Overview

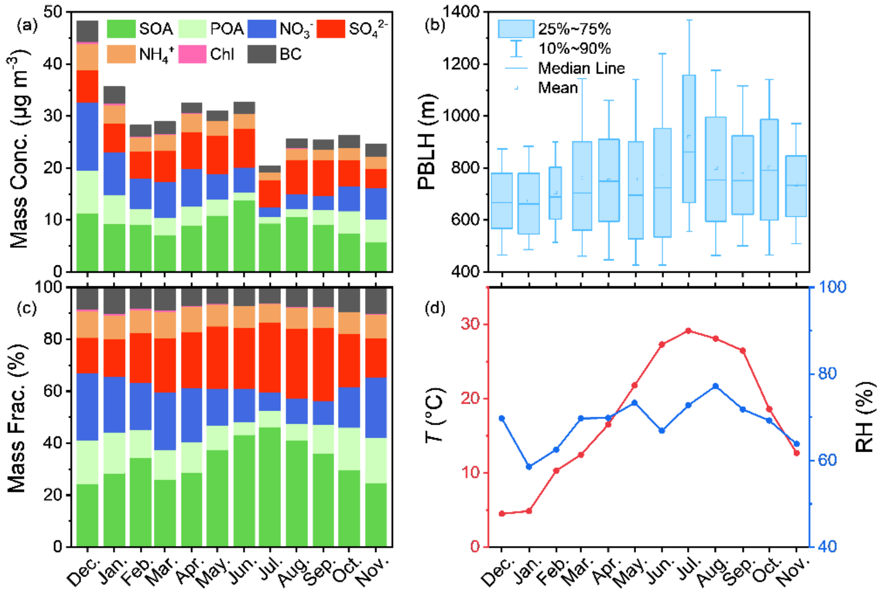

Figure 1: Monthly average (a) mass concentration and (c) mass fraction of diverse chemical components of $PM_{2.5}$. Monthly average (b) PBLH, (d) *T*, and RH.

In 3.2 Chemical composition dynamics of $PM_{2.5}$ pollution

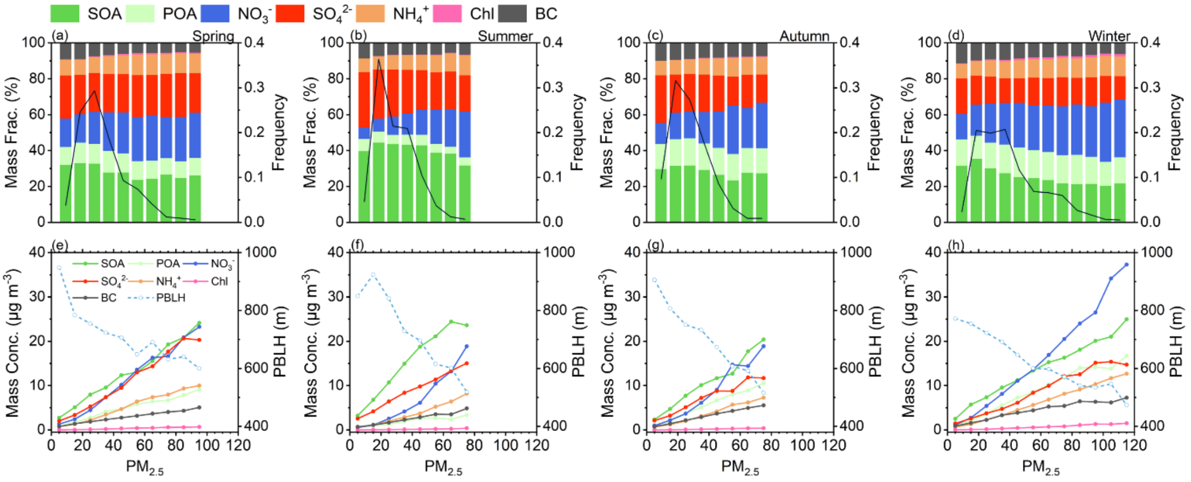

Figure 5: Mass fractions of $PM_{2.5}$ chemical components (left y axis) and frequency distribution of $PM_{2.5}$ data points relative to the total number of data points (right y-axis, black line) as a function of $PM_{2.5}$ mass concentration in (a) spring, (b) summer, (c)autumn, and (d) winter at the NUIST site. Mass concentrations of $PM_{2.5}$ chemical components (left y axis) and PBLH (right y axis, blue dashed line) as a function of $PM_{2.5}$ mass concentration in (e) spring, (f) summer, (g) autumn, and (h) winter. Data are grouped in $PM_{2.5}$ bins with 10 μg m^{-3} increments. Bins containing fewer than 10 data points are excluded.

Minor Concerns 4. At line 239 (beginning of Section 3.2: "In order to investigate…"), the text could be shortened to directly state the research objective.

Response: We have revised the opening of Section 3.2 to directly state the research objective, following the reviewer's comment to improve conciseness.

In 3.2 Chemical composition dynamics of $PM_{2.5}$ pollution

To investigate the role of different chemical components in pollution events, the distinct impacts of $PM_{2.5}$ chemical components on pollution evolution during elevated aerosol loading at the NUIST site are illustrated by Fig. 5.

Minor Concerns 5. Please clarify the calculation basis of the "Relative Change Rate" in Figure S7 to ensure reproducibility.

Response: To eliminate ambiguity and ensure reproducibility, we have refined the terminology and provided a precise definition at the beginning of section 3.4. The parameter is now explicitly referred to as the "rate of change", or "sensitivity (S_{PBLH})", of $PM_{2.5}$ chemical components with respect to PBLH. A more detailed elaboration of the formula has been provided in the main text.

In 3.4 Sensitivity of $PM_{2.5}$ chemical components to PBLH

To further study the influence of PBLH on different chemical components, the changes in $PM_{2.5}$ chemical components with decreasing PBLH across four seasons at the NUIST site are illustrated in Fig. 8e. The sensitivity of a specified chemical component to PBLH changes (S_{PBLH}) is defined quantitatively as:

$$S_{\mathrm{PBLH}} = -\frac{\Delta C}{\Delta \mathrm{PBLH}}$$

Here, S_{PBLH} specifically represents the absolute rate of change in $PM_{2.5}$ chemical components with decreasing PBLH, where ΔC is the change in mass concentration and $\Delta \mathrm{PBLH}$ is the change in PBLH. In this study, we report S_{PBLH} in units of $\mu g\ m^{-3}\ (100\ m)^{-1}$, representing the concentration change per 100 m decrease in PBLH.

References:

Kang, H., Zhu, B., de Leeuw, G., Yu, B., van der A, R. J., and Lu, W.: Impact of urban heat island on inorganic aerosol in the lower free troposphere: a case study in Hangzhou, China, Atmos. Che. Phys. , 22, 10623-10634, 10.5194/acp-22-10623-2022, 2022.

Peng, W., Zhu, B., Kang, H., Chen, K., Lu, W., Lu, C., Kang, N., Hu, J., Chen, H., and Liao, H.: Inconsistent 3-D Structures and Sources of Sulfate Ammonium and Nitrate Ammonium Aerosols During Cold Front Episodes, J. Geophys. Res.-Atmos., 129, 10.1029/2023jd039958, 2024.

Response to RC2

This manuscript presents a comprehensive one-year field observation in Nanjing to investigate the seasonal dynamics of $PM_{2.5}$ chemical components and the modulation effects of planetary boundary layer height (PBLH). The work addresses an important knowledge gap in understanding how boundary layer processes regulate aerosol composition in the Yangtze River Delta (YRD). The dataset is valuable, the research objectives are interesting and the study provides insights with both scientific and policy relevance. However, the results are largely enumerative, lacking conciseness, and the analysis of PBLH effects remains insufficiently in-depth. Therefore, several aspects of the manuscript require further clarification and strengthening before it can be considered for publication.

Major:

1. Since PBLH exerts strong quantitative influence on the results, and lidar-based retrievals of PBLH are subject to substantial uncertainties. The manuscript should explicitly discuss these uncertainties. If necessary, cross-validation with reanalysis datasets (e.g., ECMWF PBLH) could be added to enhance the credibility of the findings.

Response: We fully agree that a thorough discussion of the uncertainties associated with lidar-derived PBLH is essential for the robustness of our findings.

There are various methods for defining the PBLH, and there is no single unified definition among scientists, as each method emphasizes different physical characteristics of the PBL. For instance, the turbulent motion method identifies PBLH as the height where turbulent kinetic energy diminishes to near zero, reflecting boundary layer stability (Singh and Natesan, 2018; Kim, 2024). The dynamical method relates PBLH to wind patterns, emphasizing wind speed and geostrophic wind patterns (Mahrt et al., 1979). The thermodynamic method typically identifies PBLH by detecting discontinuities in the temperature gradient (Zhang et al., 2020). Similarly, the substance distribution method uses lidar signals to detect water vapor and aerosol gradients (Jiang et al., 2021).

The substance distribution method, where PBLH is identified as the height of the minimum gradient (Min GRD) in the backscatter coefficient profile, employed in this study is inherently consistent with the goal of investigating the relationship between PBLH and aerosol mass concentration. Despite its inherent uncertainties, this method is widely used for investigating relative changes and diurnal/seasonal trends in PBLH (Luan et al., 2018; Su et al., 2020; Han et al., 2024), which is the primary focus of our analysis. The PBLH in the ECMWF Reanalysis v5 (ERA5) is derived diagnostically from the bulk Richardson number method, integrated with numerical modeling and multi-source data assimilation (Xi et al., 2024). This approach yields a thermodynamic PBLH, the core of which is the thermal and dynamic stability of atmospheric stratification. Consequently, it may be less directly coupled to near-surface aerosol concentrations than the substance distribution method. Furthermore, as demonstrated in Han et al. (2024) using data from the same field campaign, given that thermodynamic factors are not the only contributors to vertical motion, the PBLH retrieved by MPL provides a more accurate representation of the PBL's impact on aerosols than that retrieved by Microwave Radiometer (MWR) (a thermodynamic method) (Fig. R2).

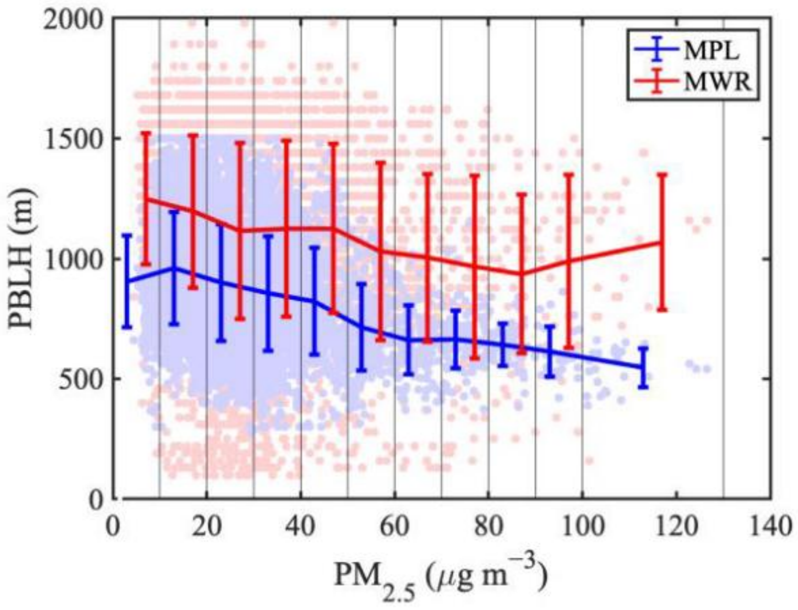

Figure R3. Light blue dots represent MPL-retrieved PBLHs and their corresponding PM$_{2.5}$ mass concentrations, and light red dots represent MWR-retrieved PBLHs and their corresponding PM$_{2.5}$ mass. concentrations. The PM$_{2.5}$ mass concentrations are categorized with a 10 μg m^{-3} difference between bins, except for the 100 to 130 μg m^{-3} bin. Mean PBLHs in each bin are then calculated. Error bars show the standard deviations in each bin. Copied from Han et al. (2024).

Nevertheless, we acknowledge the uncertainties associated with retrieving PBLH using the substance distribution method with MPL. Therefore, we have added a discussion about these limitations.

In 2.2 Instruments:

The retrieval of PBLH using this method is subject to uncertainties, primarily including interference from aerosol/cloud layers above planetary boundary layer and a blind zone below 270 m. Importantly, these uncertainties predominantly affect the absolute value of PBLH. Given that the study emphasizes the relative changes, diurnal cycles, and seasonal trends of PBLH and its correlation with aerosol composition, the conclusions remain robust.

2. The analysis of PBLH influences remains insufficiently in-depth. For example, Section 3.5 on potential source contributions appears somewhat detached from the central theme of boundary-layer effects. This section needs improvement.

Response: We agree that the original discussion on potential source contributions could be better integrated with the theme of boundary-layer effects. In response, we have thoroughly revised Section 3.5 to create an explicit and process-oriented link between the identified source regions and PBLH dynamics. The key improvement is that we now systematically use PBLH distribution data from the pollution roses to interpret the source patterns. The revised discussion explicitly states how different PBLH regimes modulate the impact of the identified source regions.

In 3.5 Source apportionment of $PM_{2.5}$ chemical components

PSCF analysis and pollution rose diagrams (Fig. 9 and 10) reveal distinct seasonal source patterns for $PM_{2.5}$ chemical components. For POA, high-potential source areas are predominantly located south of the NUIST site during spring, summer, and autumn (Fig. 9a), with elevated concentrations in the pollution roses occurring mainly at low wind speeds from southeasterly directions (Fig. 10a). This pattern suggests dominant influences from local industrial emissions. In winter, however, POA source regions expand northward to the NCP (Fig. 9a4), and the pollution roses indicate high POA concentrations at higher WS from northerly and southeasterly directions (Fig. 10a4), pointing to a combination of local emissions and long-range transport from the north (Cao et al., 2022). POA concentrations generally exhibit an inverse relationship with PBLH in the pollution roses (Fig. 10a1-a4 vs. e1-e4), highlighting the role of a lower PBLH in promoting primary aerosol accumulation. Notably, in winter, under northeasterly winds of 4–4.5 m s^{-1}, all components show peak concentrations, corresponding to a PBLH of ~570 m (Fig. 10a4-e4). Although this PBLH is not the seasonal minimum, it facilitates horizontal transport of industrial and urban pollutants from the northeast while suppressing vertical dispersion, collectively leading to heavy pollution.

Similar PSCF and pollution rose patterns for POA and SOA in summer (Figs. 9a2, b2, and 10a2, b2) imply shared emission sources, corroborating enhanced photochemical activity that drives rapid SOA formation from gaseous precursors and POA conversion under elevated temperatures. SOA's high-potential sources in summer and autumn concentrate in southeastern forested hills south of the site (Figs. 9b2 and b3), aligning with concentration maxima under southeasterly winds (Figs. 10b2 and b3). Elevated SOA under easterly winds and higher wind speeds corresponds to increased PBLH, facilitating precursor transport. This aligns with southeastern monsoon flows conveying biogenic precursors from southern forests (Wang et al., 2017). Summer SOA peaks at lower wind speeds suggest local formation alongside regional transport, whereas autumn patterns emphasize stronger transport. In winter, SOA sources expand to the NCP (Fig. 9b4), with peaks under northerly winds (Fig. 10b4). Associated higher PBLH indicates substantial long-range northern transport contributions to winter SOA.

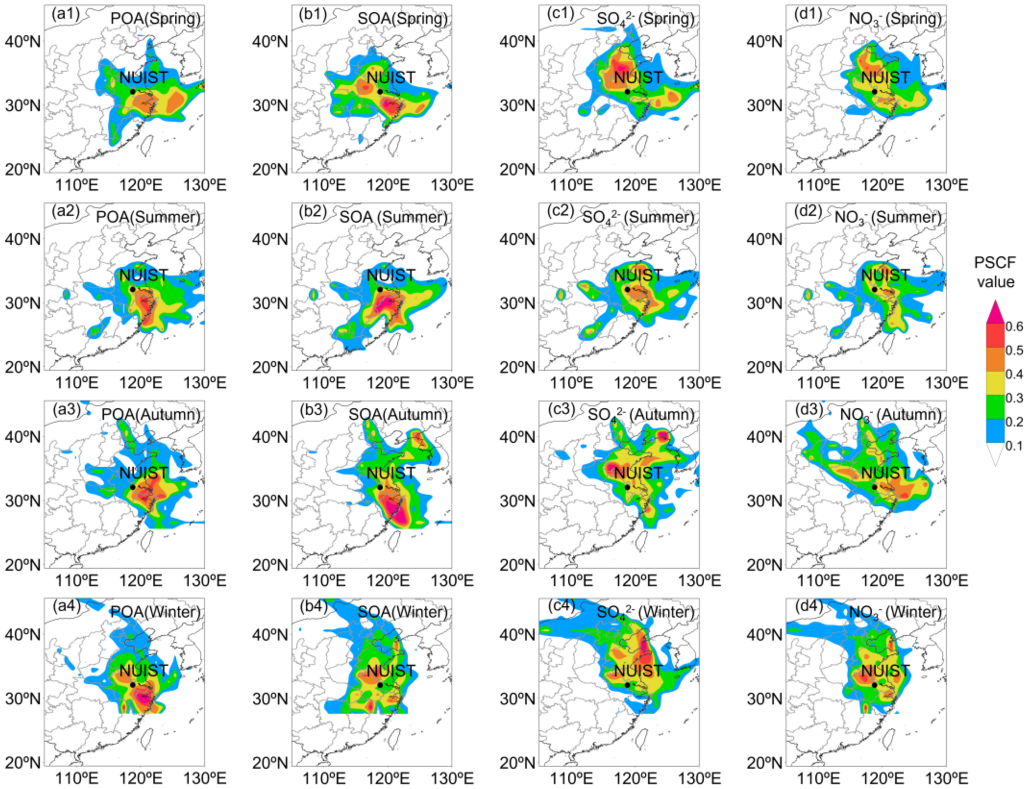

Figure 9: PSCF analysis of (a) POA, (b) SOA, (c) sulfate, and (d) nitrate in $PM_{2.5}$ during four seasons. The black dot indicates the NUIST site. The color scale indicates the values of PSCF.

Sulfate source regions predominantly localize within the YRD in summer (Fig. 9c2), with concentration maxima at low WS (Fig. 10c2), underscoring the prevalence of local photochemical formation under elevated *T*. In spring, autumn, and winter, these regions shift northward to the NCP (Fig. 9c), exhibiting more dispersed high-concentration patterns in pollution roses (Figs. 10c1, c3 and c4), indicative of enhanced regional transport. This seasonal dichotomy aligns with sulfate's diurnal patterns. Furthermore, elevated sulfate concentrations under higher WS and PBLH across all seasons reinforce the significance of long-range transport.

Nitrate source regions localize proximate to the NUIST site in summer (Fig. 9d2), with concentration maxima at low WS (Fig. 10d2), attributable to nitrate's elevated volatility and constrained transport under warm conditions. In winter, nitrate sources coincide with those of SOA (Fig. 9d4), promoted by low *T* and high RH that enhance aqueous-phase formation. Winter nitrate peaks manifest at higher WS in the pollution rose (Fig. 10d4), inversely correlating with PBLH distribution, thereby emphasizing the shallow boundary layer contribution to nitrate accumulation via inhibited vertical dispersion and expedited chemical production.

These results elucidate the interactions among local emissions, regional transport, and meteorological factors (e.g., WD, PBLH) in determining $PM_{2.5}$ chemical composition. The differentiated source patterns emphasize the imperative for tailored emission control strategies, including reductions in industrial and combustion sources within the YRD and northern provinces to attenuate winter POA and nitrate, as well as regulation of biogenic precursors to curtail summer SOA.

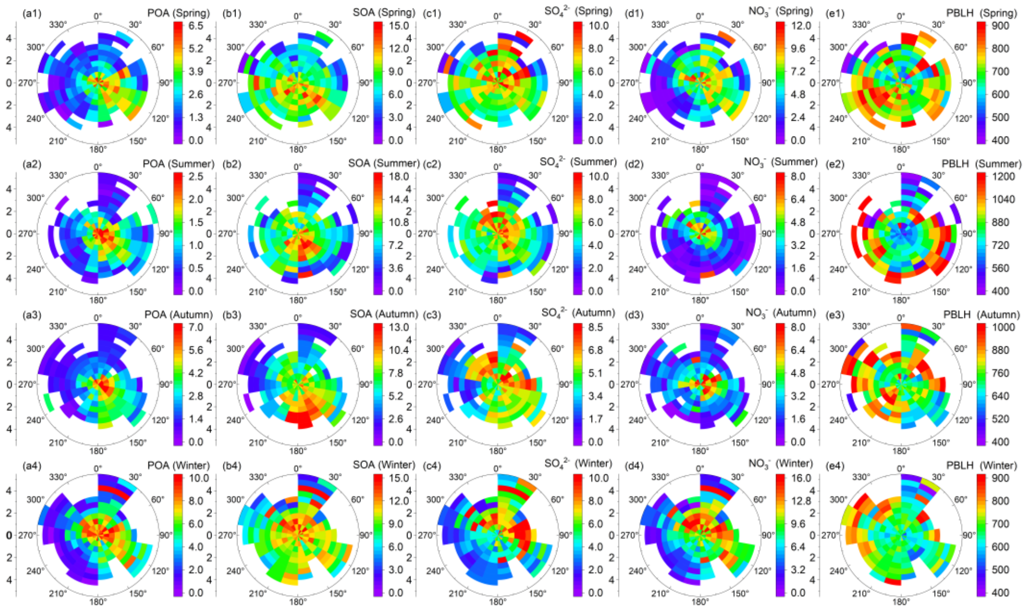

Figure 10: Pollution roses of (a) POA, (b) SOA, (c) sulfate, and (d) nitrate during four seasons. The data are grouped into grids with increments of WS and WD being 0.5 m $s^{-1}$and 20°, respectively. The unit of color scale is µg m^{-3}.

Specifics:

Specifics 1. In the Introduction, the narrative could be restructured. It is better to first present the broad scientific problem, and then narrow down to the atmospheric situation in Nanjing, rather than the current order.

Response: We fully agree that it is better to first present broad scientific problem, and then narrow down to the atmospheric situation in Nanjing. Following this advice, we have restructured the Introduction.

The introduction now begins by outlining the broad public health and environmental challenges posed by $PM_{2.5}$ globally. It then reviews the current research on the various components of $PM_{2.5}$ and the impact of Planetary Boundary Layer Height (PBLH) on these components. Subsequently, the focus is narrowed down to the regional context of the Yangtze River Delta (YRD) and its specific pollution challenges. Finally, it identifies the specific research gap related to the interaction between aerosol chemistry and PBLH in Nanjing, which our study aims to address. We believe this revised structure provides a much clearer and more compelling rationale for our research.

In 1 Introduction

Fine particulate matter ($PM_{2.5}$), defined as particles with an aerodynamic diameter less than 2.5 μm, is a major environmental and public health concern due to its adverse effects on air quality, visibility, and human health. Exposure to $PM_{2.5}$ has been linked to increased risks of respiratory and cardiovascular diseases, premature mortality, and reduced life expectancy (Pui et al., 2014; Beelen et al., 2015). The major components of $PM_{2.5}$ include organic aerosol (OA), inorganic ions such as nitrate (NO_3^-), sulfate (SO_4^{2-}), ammonium (NH_4^+), chloride (Chl), and black carbon (BC). Each of these components arises from distinct sources and formation pathways. For example, BC is emitted directly from incomplete combustion of fossil fuels and biomass, while nitrate and sulfate are typically formed through secondary chemical processes involving the oxidation of nitrogen oxides (NO_X) and sulfur dioxide (SO_2), respectively.

Secondary inorganic aerosols exhibit strong seasonal dependencies. Nitrate formation is particularly enhanced during cold and humid seasons, as low T and high RH promote heterogeneous reactions, especially the hydrolysis of nitrogen pentoxide (N_2O_5) on aerosol surfaces (Wang et al., 2015). These reactions are more efficient under stable winter meteorology, leading to elevated nitrate concentrations in many mid- and high- latitude continental regions (Alexander et al., 2020). In contrast, sulfate formation occurs via both gas-phase oxidation (primarily by OH radicals) and aqueous-phase pathways involving oxidants such as hydrogen peroxide (H_2O_2), ozone (O_3), and nitrogen dioxide (NO_2). The aqueous-phase route tends to dominate under high RH and cloud presence, especially in summer, when photochemistry enhances the production of oxidants (Zhang et al., 2016; Liu et al., 2021). Thus, sulfate exhibits a different seasonal pattern, often peaking in warm, humid, and photochemically active periods. Ammonium, as a crucial role of neutralizing agent, regulates aerosol acidity and modulates the gas-particle partitioning of nitrate and sulfate (Wang et al., 2016; Xian et al., 2023)

Organic aerosols, especially secondary organic aerosols (SOA), present additional complexity due to their wide variety of precursors and formation mechanisms. Source apportionment of OA is commonly achieved using statistical tools such as positive matrix factorization (PMF) and the multilinear engine (ME-2), which deconvolute time-resolved mass spectra into distinct factors associated with sources or processes (Ulbrich et al., 2009; Canonaco et al., 2013). High-resolution instruments like the aerosol chemical speciation monitor (ACSM) and aerosol mass spectrometer (AMS) have been widely used to study aerosol chemical composition. For example, Zhang et al. (2017) reported that during autumn in Nanjing, primary organic aerosol (POA) in $PM_{2.5}$ originates from traffic, cooking, and biomass burning, while SOA formation is driven by RH. In contrast, summertime SOA formation in rural Yangtze River Delta (YRD) areas is largely photochemically driven (Huang et al., 2020). These findings highlight the strong seasonal and spatial variability of both organic and inorganic $PM_{2.5}$ components.

The planetary boundary layer height (PBLH) is a key meteorological parameter that influences pollutant dispersion and vertical mixing. A well-established negative correlation exists between PBLH and near-surface $PM_{2.5}$ concentrations (Minoura and Shimo, 2011; Wang et al., 2018; Han et al., 2024). Under low PBLH and stagnant conditions, primary pollutants such as BC and POA can accumulate rapidly. Meanwhile, secondary aerosols respond more dynamically to PBLH due to their dependence on atmospheric oxidation, humidity, and solar radiation. For instance, low PBLH in winter exacerbates BC accumulation in the YRD (Lu et al., 2019), while high PBLH in the North China Plain (NCP) facilitates SO_2-to-sulfate conversion, and low PBLH promotes nitrate enrichment (Si et al., 2019). In southern cities like Guangzhou, high PBLH promotes SOA formation by enhancing O_3 transport and particle-phase oxidation processes (Li et al., 2024).

In recent decades, rapid industrialization and urbanization in China have exacerbated $PM_{2.5}$ pollution, especially in highly developed regions such as the YRD. As one of the most densely populated and economically active areas in China, the YRD suffers from frequent haze episodes and elevated $PM_{2.5}$ levels. Nanjing, a key city in the YRD, serves as a representative urban environment where $PM_{2.5}$ pollution displays complex seasonal variations and diverse chemical composition. Numerous studies have highlighted that $PM_{2.5}$ in this region is influenced by both local sources and regional transport, modulated by meteorological factors such as temperature (T), relative humidity (RH), and wind patterns (Sun et al., 2015; Zhu et al., 2021) Thus, Nanjing serves as an ideal representative region for understanding the complex interactions between emissions, atmospheric processes, and meteorology in the YRD.

Research on the seasonal and spatial variability of $PM_{2.5}$ components has advanced. Remote sensing technologies, such as micro-pulse lidar (MPL), now enable high-resolution PBLH estimation based on aerosol backscatter profiles (Su et al., 2020; Han et al., 2024; Yang et al., 2025). However, many studies focus on bulk $PM_{2.5}$ mass or limited chemical species, often rely on simulation data and some studies feature short observation periods. There remains a need for comprehensive, long-term and high-temporal-resolution observational studies in the YRD that resolve the full chemical profile of $PM_{2.5}$ and quantify its modulation by planetary boundary layer processes across seasons especially under current emission control policies.

To address these gaps, this study conducted a comprehensive one-year field campaign in Nanjing from December 2020 to November 2021. Continuous online measurements of $PM_{2.5}$ chemical components and PBLH are obtained using a quadrupole aerosol chemical speciation monitor (Q-ACSM), aethalometer, and MPL. The objectives are to (1) characterize the seasonal and diurnal variations of $PM_{2.5}$ chemical components, (2) quantify the influence of PBLH on component-specific mass concentrations, and (3) identify potential source regions using positive matrix factorization and potential source contribution function (PSCF) analysis.

Specifics 2. Lines 69-70: The statement "Comprehensive, long-term observational studies ··· are still lacking in the YRD" is somewhat overstated. Relevant studies exist, so this should be rephrased more cautiously.

Response: We agree that the original wording was too absolute and could be misinterpreted. We have revised the sentence to more accurately reflect the state of research, specifically highlighting that studies focusing on the interplay between chemical composition and planetary boundary layer processes are limited, which is the key gap our research aims to fill.

In 1 Introduction

However, many studies focus on bulk $PM_{2.5}$ mass or limited chemical species, often rely on simulation data and some studies feature short observation periods. There remains a need for comprehensive, long-term and high-temporal-resolution observational studies in the YRD that resolve the full chemical profile of $PM_{2.5}$ and quantify its modulation by planetary boundary layer processes across seasons especially under current emission control policies.

Specifics 3&4. Lines 90-93: The Introduction should not present conclusions, it should focus on research objectives and study plan.

Lines 94-99: Introducing each section by restating its content is meaningless.

Response: We completely agree that the Introduction section should be forward-looking and focus on stating the research gaps and objectives, rather than presenting conclusive findings. In response, we have revised the concluding paragraph of the Introduction section. The conclusive sentences (Lines 90-93) and the formulaic overview of each section (Lines 94-99) have been deleted from the manuscript. The Introduction is now more concise and focused on stating the research objectives.

Specifics 5. Lines 217-223: The correlation analysis with temperature and PBLH could also include primary species, such as BC, not only POA.

Response: We thank the reviewer for this insightful suggestion. We have now performed correlation analysis for all chemical components.

Figure R3 presents the scatter plots of monthly average mass concentrations for all components against monthly average PBLH and temperature, along with their linear regression lines. Figure R4 compares the slopes and correlation coefficients (*R*) of these linear fits.

Analysis of Fig. R4 indicates that despite notable correlations, the fitted slopes for POA, BC, ammonium and chloride are significantly smaller than those for SOA, sulfate, and nitrate, pointing to a weaker absolute response to meteorological changes.

To maintain a clear and concise narrative, Figure 4 in the main text highlights SOA, sulfate, and nitrate. This selective presentation aligns with the primary focus of our study: the dynamic response of secondary aerosol formation to meteorological drivers.

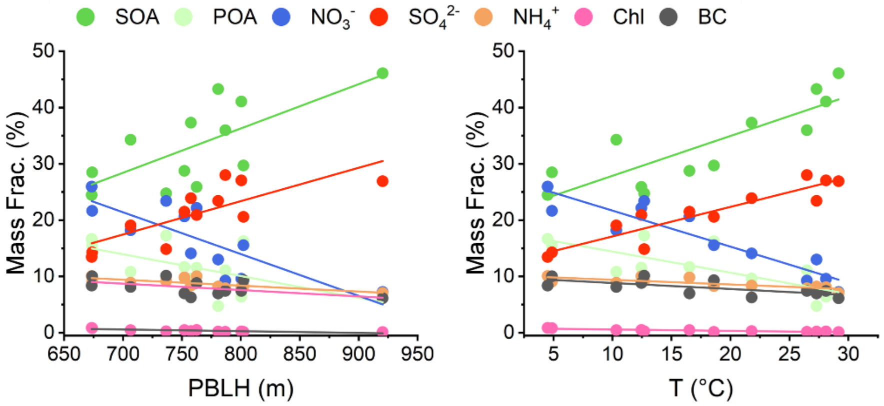

Figure R4 The correlation and linear fitting lines between the monthly average mass fractions of SOA, POA, sulfate, nitrate BC, ammonium and chloride in $PM_{2.5}$ and the corresponding monthly average (a) PBLH and (b) *T*.

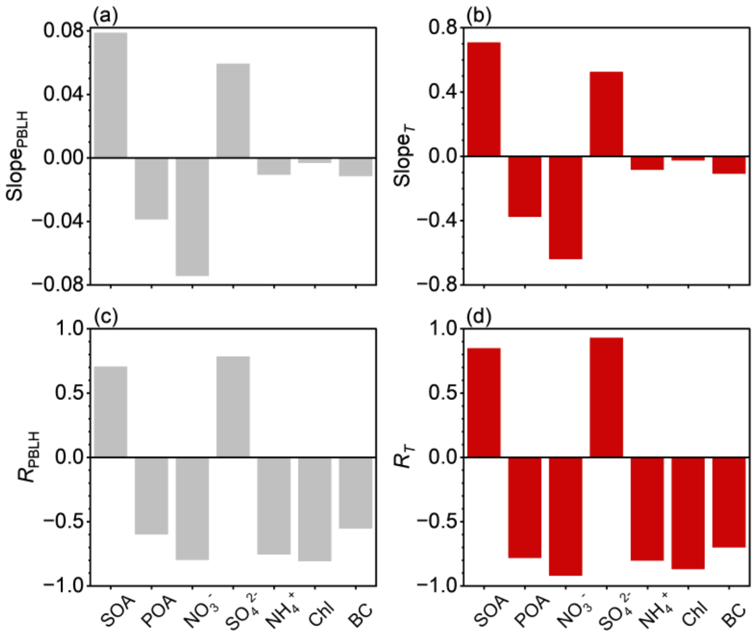

Figure R5 The slopes and correlation coefficients of the linear fitting lines between the monthly average mass fractions of chemical components in $PM_{2.5}$ and the monthly average (a)(c) PBLH and (b)(d) *T*.

In 3.1 Overview

To investigate the dynamic responses of the formation and accumulation processes of highly responsive secondary chemical components to meteorological factors, the relationships between the monthly average mass fractions of chemical components in $PM_{2.5}$ and monthly average *T* and PBLH are analysed (Fig. 4 and S6). It is found that the monthly average mass fractions of SOA, sulfate, and nitrate show strong *T* dependencies (Fig. 4a), with correlation coefficients of $R_{SOA\text{-}T}$ = 0.86 (positive), $R_{SO_4^{2-}\text{-}T}$ = 0.93 (strong positive), and $R_{NO_3^-\text{-}T}$ = -0.92 (strong negative) with monthly average *T*.

Specifics 6. In Fig. 4b, one conspicuously high PBLH data point appears to drive much of the correlation. If this point were excluded, would the correlation still remain as strong? Would the influence of the PBLH not be as significant?

Response: We thank the reviewer for raising this important point. We have carefully examined the potential influence of the highest PBLH data point occurred in the warmest month (July) shown in Fig. 4b on the correlation analysis.

Figure R5 presents a comparison of the scatter plots with and without this point included, while Figure R6 provides a more detailed comparison of the corresponding slopes and R. As shown, after excluding this point, nitrate (R = -0.75) and sulfate (R = 0.83) maintain strong correlations with PBLH (Fig. R6a). For SOA, while the absolute value of the correlation coefficient decreases, it remains within a moderate range. Critically, the slopes of the linear fits show little change before and after the exclusion of the high PBLH point (Fig. R6b). This indicates that the overall influence of PBLH is robust and not unduly dependent on the highest PBLH data point.

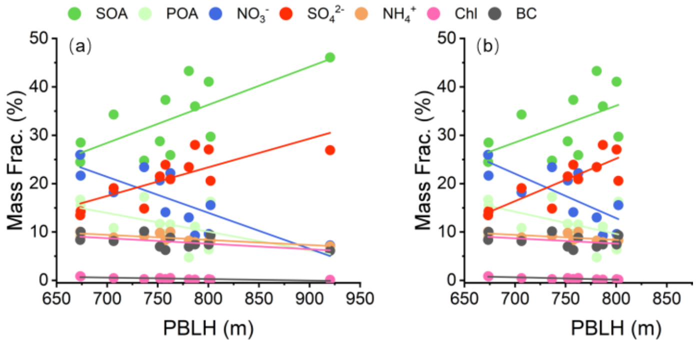

Figure R6 The scatter plots and the linear fitting lines between monthly average mass fractions of chemical components in $PM_{2.5}$ and PBLH (a) before and (b) after the exclusion of the highest PBLH point (i.e., the data from July).

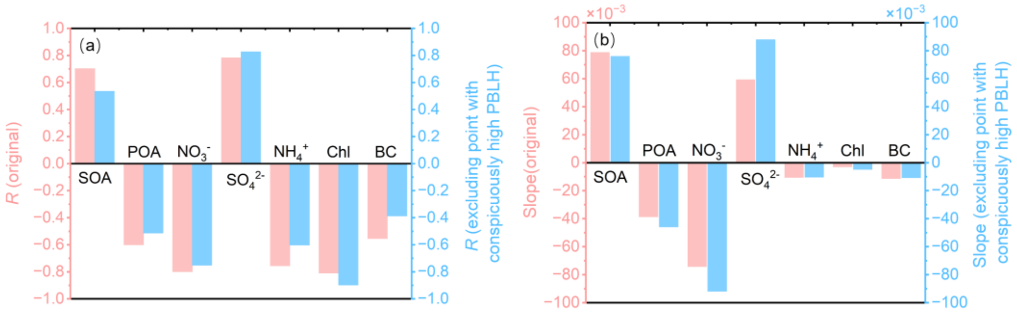

Figure R7 (a) R and (b) slopes of the linear fitting lines between monthly average mass fractions of chemical components in $PM_{2.5}$ and PBLH before and after the exclusion of the highest PBLH point.

Furthermore, this highest PBLH data point corresponds to a typical deep boundary layer condition observed in July (summer) and constitutes a valid observation reflecting real atmospheric conditions. Arbitrarily removing it could introduce bias and weaken the representativeness of the dataset. We therefore elected to retain this point in our analysis to comprehensively capture the natural variability of PBLH.

A statement explaining and justifying the inclusion of this specific highest PBLH point has been added to the main text.

In 3.1 Overview

Note that the PBLH value of 920 m in Fig. 4b represents a typical summertime observation from July and is physically consistent with seasonal boundary layer development. As a valid data point, its inclusion does not change the core finding of a differential PBLH impact on secondary aerosols (Fig. S7).

Specifics 7. The use of the [concentration] × PBLH method to eliminate dilution effects requires justification, has this approach been adopted in previous studies? If so, relevant references should be cited. If not, how reliable is it in this context?

Response: We agree that the use of the [component] × PBLH method deserves careful justification. We greatly appreciate the opportunity to clarify the rationale and justification for our adoption of this method.

While the direct multiplication of chemical component concentrations by PBLH is not a standard convention in literature, this approach is grounded in physics. The rise and fall of the PBLH determines the atmospheric volume near the surface, and its widespread significant negative correlation with $PM_{2.5}$ mass concentrations has been consistently confirmed by numerous studies (Minoura and Shimo, 2011; Su et al., 2018; Lv et al., 2020). To remove the dilution effect of PBLH variations, this study employs [component] × PBLH to approximate the aerosol loading within the boundary layer. The primary objective of this approach is to separate changes driven by emissions and chemical processes from the variation dominated by physical dilution driven by PBLH variations.

To verify the reliability of this approach, we compared its results with an established alternative—normalizing chemical component concentrations by the concentration of CO (Kuang et al., 2020). Although long-term, online CO measurements were not part of this campaign, thus the data used were obtained from the Maigaoqiao site of the China National Environmental Monitoring Centre (CNEMC, https://air.cnemc.cn:18014/), the diurnal variation trends of various components derived from the two methods show strong consistency (Fig. R7 and R8). This agreement demonstrates that the [component] × PBLH method effectively achieves its intended purpose of isolating the dilution effect.

Compared to the CO normalization method, directly using synchronously observed PBLH data for correction is more straightforward and avoids potential biases arising from inconsistent emission sources between CO and the chemical components. Although few existing studies have employed an identical mathematical formulation, our approach is based on clear physical reasoning and is supported by cross-validation with an alternative method, confirming its reliability in this study.

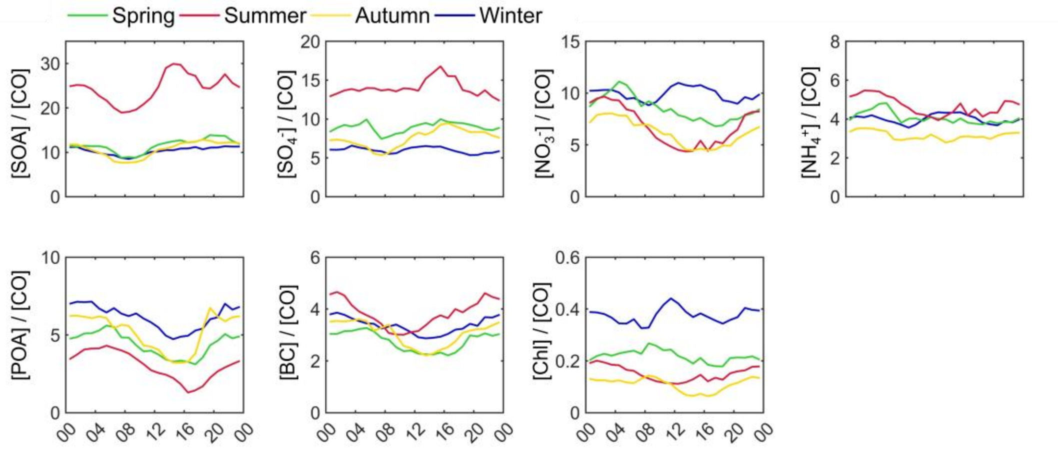

Figure R8 Average diurnal variations of mass concentrations of $PM_{2.5}$ chemical components divided by CO concentration (denoted as [component]/[CO].

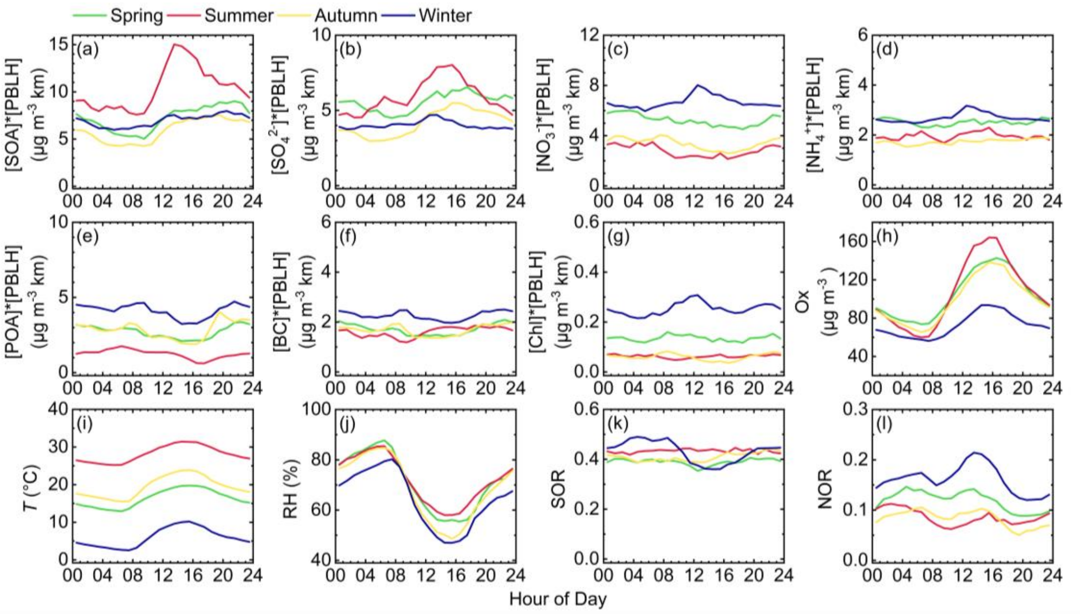

Figure R9 Average diurnal variations of (a–g) $PM_{2.5}$ chemical components after removing the dilution effect of planetary boundary layer, (h) photochemical oxidant (O_X), (i) *T*, (j) RH, (k) sulfate oxidation ratio (SOR), and (l) nitrogen oxidation ratio (NOR) during four seasons. To isolate emission sources and secondary formation effects on local pollution, the average diurnal variations of $PM_{2.5}$ chemical components are multiplied by PBLH to remove the dilution effect (denoted as [component]*[PBLH], e.g., [POA]*[PBLH], [BC]*[PBLH]) in a–g panels.

A new statement has been added to the main text to clarify the principle and limitations of this approach.

In 3.3 Diurnal dynamics of $PM_{2.5}$ chemical components

PBLH significantly modulates the diurnal variations of $PM_{2.5}$ chemical components. Previous studies often use the ratio of aerosol mass concentrations to CO concentrations to assess the dilution effect of PBLH variations (e.g., Kuang et al., 2020). However, this approach assumes CO variability is solely driven by PBLH fluctuations, overlooking emission source variations. To address this limitation, high-temporal-resolution PBLH data from the MPL are utilized. To isolate emission sources and secondary formation effects on local pollution, [component]*PBLH is employed to approximate the aerosol loading within the boundary layer in this study, thereby removing the dilution effect. It is important to note that while the absolute value of this parameter is not a direct physical measurement, its diurnal evolution provides valuable insights for investigating source processes and chemical mechanisms.

Specifics 8. In Section 3.4, simply describing higher or lower pollutant concentrations may not adequately represent "sensitivity." It should be clarified whether sensitivity refers to the magnitude of concentration change with PBLH variations, rather than absolute concentration levels.

Response: We completely agree that a rigorous discussion of "sensitivity" should be based on the rate of change in concentration with respect to PBLH, not merely on absolute concentration levels.

In response to this comment, we have revised Section 3.4 to clarify the definition of sensitivity. We now explicitly define the sensitivity at the beginning of the section as the rate of change in the mass concentration of chemical components for every 100 m decrease in PBLH.

The analysis now focuses on comparing these rates of change between different chemical components. The figure S7 previously shown in Supplementary has been removed, and four new subplots have been incorporated into Figure 8 of the main text. Additionally, revisions have been made to the descriptions related to sensitivity in Section 3.4.

In 3.4 Sensitivity of $PM_{2.5}$ chemical components to PBLH

To further study the influence of PBLH on different chemical components, the changes in $PM_{2.5}$ chemical components with decreasing PBLH across four seasons at the NUIST site are illustrated in Fig. 8e. The sensitivity of a specified chemical component to PBLH changes (S_{PBLH}) is defined quantitatively as:

$$S_{\mathrm{PBLH}} = -\frac{\Delta C}{\Delta \mathrm{PBLH}}$$

Here, S_{PBLH} specifically represents the absolute rate of change in $PM_{2.5}$ chemical components with decreasing PBLH, where ΔC is the change in mass concentration and ΔPBLH is the change in PBLH. In this study, we report S_{PBLH} in units of $\mu g\ m^{-3}\ (100\ m)^{-1}$, representing the concentration change per 100 m decrease in PBLH.

As PBLH decreases, the S_{PBLH} of POA is higher than that of BC within the 300–900 m PBLH range (Fig. 8a3-d3), suggesting that the concentration of POA increases at a faster rate with the lowering of the PBLH than do those of BC.The total contribution of primary aerosols (POA, BC, and chloride) to $PM_{2.5}$ increases across all seasons as PBLH declines (Fig. 8a1-d1), reflecting the enhanced accumulation of locally emitted primary aerosols under low PBLH conditions.

In spring, $PM_{2.5}$ chemical components display complex relationships with PBLH. Notably, SOA and sulfate mass concentrations are anomalously lower under low PBLH (300–500 m) than at higher PBLH (500–700 m) (Fig. 8a2). Further analysis reveals that, at PBLH between 300 and 500 m, lower WS ($1.6\ m \cdot s^{-1}$), lower T (15.0°C), higher RH (92.3%) and higher frequency of nighttime occurrences suppress the photochemical formation and accumulation of SOA and sulfate, counteracting accumulation effects of low PBL. In contrast, nitrate mass concentrations are significantly affected by the accumulation effect at low PBLH in spring, exhibiting a negative correlation with PBLH.

In summer and autumn, pronounced diurnal differences in PBLH influence component dynamics. Sulfate and SOA dominate $PM_{2.5}$ pollution during daytime under high PBLH and elevated T (Fig. 8b1 and b2), but their mass fractions decrease as PBLH declines. Nitrate exhibits the opposite trend, with mass concentrations surging by 331.0% in summer and 313.0% in autumn as PBLH decreases, far exceeding increases in sulfate (56.0% in summer, 21.0% in autumn) and SOA (25.0% in summer, 44.0% in autumn, Fig. 8b2 and c2). As noted in Sect. 3.2, sulfate and SOA prevail during low-pollution, high-PBLH episodes, while nitrate dominates during high-pollution, low-PBLH episodes. However, summer heatwaves reduce the thermal stability of ammonium nitrate, such that nitrate's dominance is limited to low-PBLH periods only in autumn. In contrast to SOA and sulfate, which generally exhibit lower S_{PBLH} across the PBLH range, nitrate shows consistently higher sensitivity (Fig. 8b3 and c3). This indicates that although low PBLH restricts vertical pollutant dispersion, sulfate and SOA, primarily driven by photochemical processes, are more sensitive to T and solar radiation than to PBLH variations.

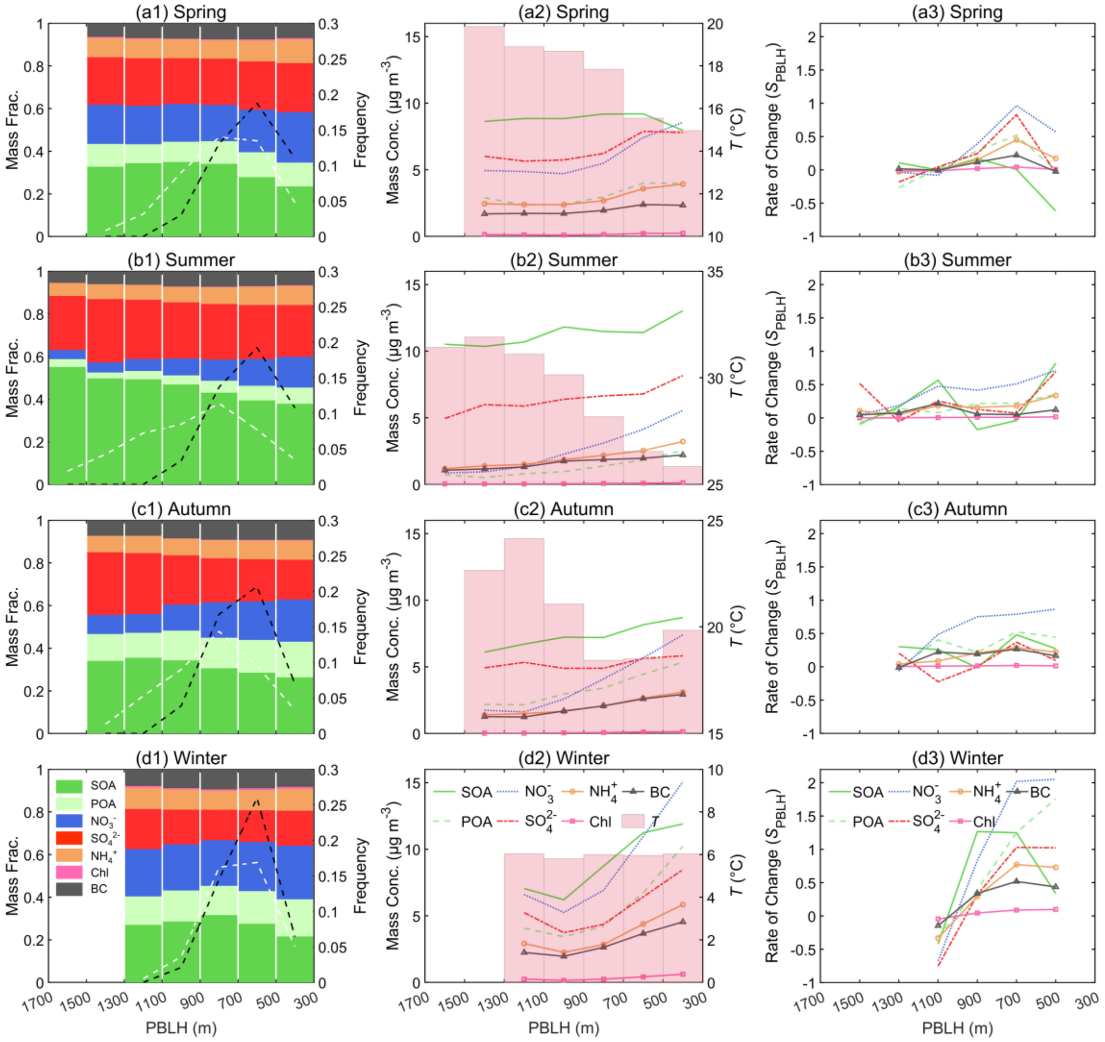

Figure 11: (a1-d1) The mass fraction of $PM_{2.5}$ chemical components as a function of PBLH distribution (left y axis) and frequency distribution of PBLH data points relative to the total number of data points (right y axis, white dashed line represents daytime and black dashed line represents nighttime) in four seasons. (a2-d2) The mass concentration of $PM_{2.5}$ chemical components (left y axis) and the T (right y axis, pink columns) as a function of PBLH distribution in four seasons. (a3-d3) The rate of change in $PM_{2.5}$ chemical components (S, units: μg m^{-3} (100 m)$^{-1}$) with the decrease of PBLH in four seasons. The data are grouped in PBLH bins with 200 m increments. Bins with the number of data points fewer than 10 are excluded.

In winter, all aerosol chemical components exhibit heightened sensitivity to PBLH. As PBLH decreases, both the rise in mass concentration and the S_{PBLH} are significantly greater than in other seasons (Fig. 8d2, d3). Nitrate shows the greatest sensitivity to PBLH, with its S_{PBLH} reaching a peak value exceeding 2. Within the 300–500 m PBLH range, nitrate constitutes 25.0% of $PM_{2.5}$, emerging as the dominant component (Fig. 8d1).The consistently low *T* (~6°C) across all PBLH intervals (Fig. 8d2) fosters conditions conducive to thermodynamic stability of ammonium nitrate (Kang et al., 2022). As illustrated in Fig. S8d, low PBLH conditions are associated with elevated RH and reduced WS. This humid environment markedly enhances nitrate formation through heterogeneous pathways, such as N_2O_5 hydrolysis (Peng et al., 2024). Simultaneously, low PBLH limits the vertical diffusion of precursors, leading to their accumulation near the surface and further boosting chemical production efficiency. The pronounced sensitivity of nitrate highlights the critical need for proactive emission control measures to avert the swift escalation of severe pollution episodes in winter.

In summary, PBLH regulates $PM_{2.5}$ chemical components through its influence on aerosol dispersion and interactions with temperature, photochemical reactions, and regional transport processes. POA shows greater sensitivity to PBLH variations than BC. In spring, reduced temperatures at low PBLH constrain SOA and sulfate formation, counteracting accumulation effects. In summer and autumn, SOA and sulfate are less sensitive to PBLH due to photochemical dominance, while nitrate exhibits heightened sensitivity. In winter, low PBLH and cold temperatures amplify the sensitivity of all components. Nitrate exhibits the highest sensitivity to PBLH across all seasons, with particularly pronounced effects under low PBLH conditions in winter. Its rapid accumulation during this period is primarily fueled by the high humidity linked to low PBLH, which vigorously promotes heterogeneous reactions like N_2O_5 hydrolysis. At the same time, the sustained low temperatures ensure the thermodynamic stability required for nitrate to persist in the particulate phase.

Specifics 9. Lines 354-355: The statement "As PBLH decreases, the average mass concentration of POA … exceeds that of BC, suggesting POA is more sensitive …" is unclear. POA concentrations are higher than BC in Figure 8. Therefore, what is meant by "exceeds" here? Is it referring to the rate of change with PBLH? This needs clarification.

Response: We thank the reviewer for pointing out this lack of clarity. The fact that POA concentrations are higher than BC does not, by itself, indicate a greater sensitivity to PBLH. We apologize for this lack of clarity.

We intended to convey that the rate of concentration increase as PBLH decreases is greater for POA than for BC, indicating that POA is more sensitive to PBLH variations.

To clarify, we have added the rate of change in the mass concentration of chemical components for every 100 m decrease in PBLH. (i.e., the sensitivity) across the four seasons in Figure 8(a3–d3). We have revised the sentence in the manuscript (Lines 354-355). This revision explicitly states that we are comparing the sensitivity (rate of change) rather than the absolute concentration, and it directly references the supporting evidence in Figure 8.

In 3.4 Sensitivity of $PM_{2.5}$ chemical components to PBLH

As PBLH decreases, the S_{PBLH} of POA is higher than that of BC within the 300–900 m PBLH range (Fig. 8a3-d3), suggesting that the concentration of POA increases at a faster rate with the lowering of the PBLH than do those of BC.

Reference:

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Response to RC3

This article analyzed the year-long observations of chemical components of fine particulate matter and their association with PBLH across seasons. The study offered valuable insight from the perspective of observational data. My general concern is the representativeness of single site for the discussion of suburban Nanjing and the generalization to the regional and spatial patterns. I am also concerned about the novelty of the paper mainly showing the effects of PBLH as a vertical dispersive term on $PM_{2.5}$ concentrations, which was shown by various prior studies.

General Comments

General Comments 1. The descriptive statements from this study are from single observational site. How representative is it for the suburban Nanjing and the pollution pattern in the YRD region? Are there any other or prior site observations can be gathered to the plot for representativeness?

Response: We thank the reviewer for raising the important question regarding the representativeness of our single-site observations. We acknowledge the inherent limitations of a single site in capturing spatial heterogeneity. Below, we clarify why NUIST site and findings remain representative of the YRD region.

The NUIST site is situated in Nanjing's northern suburbs, within the highly urbanized YRD cluster, and acts as a key convergence zone for regional pollution. Its location enables capturing mixed influences from urban, industrial, and regional transport emissions, making it a representative site for studying complex pollution processes in the YRD (Wang et al., 2016; Song et al., 2023) .

The annual average and seasonal variations in $PM_{2.5}$ concentrations at the NUIST site in our study are similar to observations in Shanghai located in the east YRD (Fu et al., 2020). Furthermore, the trends of nitrate and sulfate concentrations with increasing $PM_{2.5}$ mass are consistent with those reported in Shanghai. The diurnal patterns and fractional contributions of OA, nitrate, sulfate, ammonium, and chloride also align well with winter measurements from Ningbo (Huang et al., 2021), and summer measurements in Nanjing (Wang et al., 2022; Xian et al., 2023). Seasonal mass spectral profiles and time series of OA factors (Fig. S2) align with those reported by Zhang et al. (2017) measured at another site in Nanjing.

While the absolute concentrations may vary spatially, the core of our study lies in revealing the response patterns of chemical components to PBLH and their seasonal source characteristics. These patterns are governed by fundamental physical and chemical mechanisms that operate similarly across the YRD under comparable meteorological conditions. Thus, our conclusions are applicable to understanding air pollution in similar environments within the region.

General Comments 2. A long-term observation usually refers to multi-year observation. I would suggest changing the title to be “year-long” or something equivalent to avoid overstatement.

Response: We acknowledge that "long-term" could be misinterpreted and that "year-long" provides a more precise description of our one-year dataset. We have accepted this suggestion and changed the title throughout the manuscript to “Measurement report: Insights into seasonal dynamics and planetary boundary layer influences on aerosol chemical components in suburban Nanjing from a one-year observation”

In title:

Measurement report: Insights into seasonal dynamics and planetary boundary layer influences on aerosol chemical components in suburban Nanjing from **one-year** observation

General Comments 3. For the potential source contributions, how can the regional receptor with the grid cells at 1 by 1 degree resolution inform the source contributions of the single site?

Response: We thank the reviewer for this insightful comment regarding the spatial resolution used in our PSCF analysis.

The PSCF method is designed to identify broad regional source areas rather than pinpoint exact emission points. The 1° × 1° grid resolution is a widely adopted standard in receptor modeling studies (Han et al., 2021; Zhao et al., 2026). This scale can effectively highlight large-scale source regions such as industrial zones or urban agglomerations without implying a false sense of precision.

However, to directly address the reviewer's concern and to rigorously test the sensitivity of our results to the choice of grid resolution, we have now performed an additional PSCF analysis using a finer 0.5° × 0.5° grid. The results show that the spatial patterns of high-potential source areas are remarkably consistent between the two resolutions (Fig. R9 and R10). The key source regions we identified remain robust, confirming that our main conclusions are not sensitive to the grid cell size.

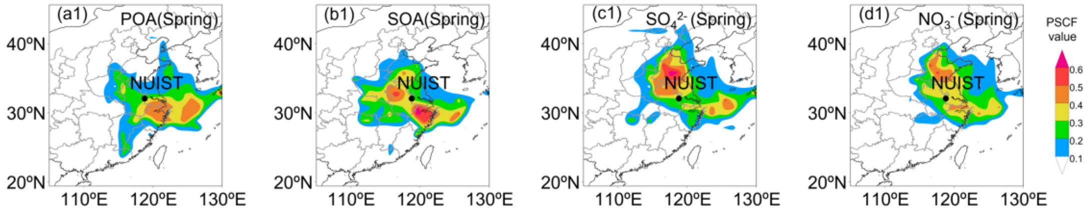

Figure R10: PSCF analysis of (a) POA, (b) SOA, (c) sulfate, and (d) nitrate in $PM_{2.5}$ in spring. The black dot indicates the NUIST site. The color scale indicates the values of PSCF. The study domain is divided into 1° × 1° grid cells.

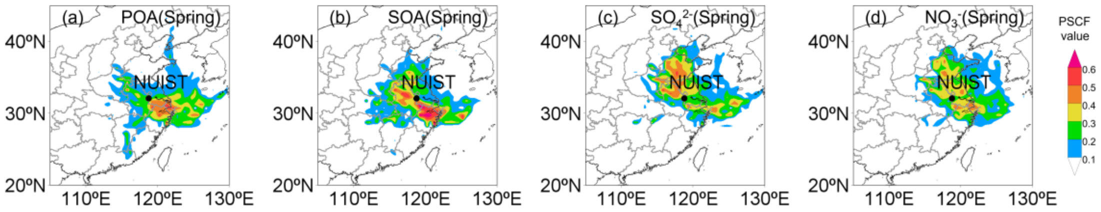

Figure R11: PSCF analysis of (a1) POA, (b1) SOA, (c1) sulfate, and (d1) nitrate in $PM_{2.5}$ in spring. The black dot indicates the NUIST site. The color scale indicates the values of PSCF. The study domain is divided into 0.5° × 0.5° grid cells.

General Comments 4. The effects of PBLH on the concentrations of $PM_{2.5}$ is overinterpreted. PBLH is only a vertical dispersive term, while the concentrations of primary aerosols are governed by their emissions, and the concentrations of secondary aerosols are governed by their chemical mechanisms. PBLH would only modulate the surface concentrations temporarily without changing the aerosol vertical burden.

Response: We thank the reviewer for this insightful comment, which allows us to clarify the role of PBLH in our study. We fully agree that PBLH acts as a vertical dispersive term in principle, and that the fundamental sources of aerosols lie in emissions and chemical processes. However, our study focuses on explaining the observed variability in near-surface mass concentrations, which is the primary metric for air quality, public health, and regulatory standards. In this context, PBLH plays a critical role. This is strongly supported by the well-established and repeatedly observed anti-correlation between PBLH and $PM_{2.5}$ concentrations vc(Su et al., 2018; Lv et al., 2020; Su et al., 2020).

While the aerosol vertical burden might remain relatively constant in the short term, the compression or expansion of this burden into a shallow or deep near-surface layer can lead to significant changes in mass concentrations. More importantly, PBLH is not an independent variable in the real atmosphere. It is coupled with the emissions and chemical mechanisms by the reviewer. Low PBLH conditions are intrinsically linked to stable meteorological conditions (low WS, temperature inversions, high RH), which suppress the dispersion of primary emissions, leading to their accumulation. These conditions also facilitate the chemical formation of pollutants. As noted in Section 3.4, for example, nitrate exhibits an enhanced heterogeneous formation under low PBLH and stable meteorological conditions.

PBLH is more appropriately defined in this study as a key environmental parameter. It directly determines the spatial volume for pollutant diffusion and is also highly correlated with meteorological conditions that influence formation mechanisms of secondary aerosols. Our analysis examines how this integrated parameter differentially affects various components, providing actionable insights for the prediction and management of air pollution events.

Specific Comments

Specific Comments 1. Line 166-167, what is the vertical height of the receptor grid cells? How would it compare with the height of the observation site?

Response: We thank the reviewer for this question. Given that our observation site is located at an altitude of 22 m above sea level, the selected receptor height of 300 m (stated in section 2.4) is well above the surface layer and the immediate influence of ground obstacles. This height represents air masses in the lower mixed layer, effectively characterizing regional transport pathways while minimizing the distortion caused by near-surface friction and very local, ground-level emissions (Polissar et al., 2001). It thus provides a robust representation of the synoptic-scale and mesoscale flows influencing our site.

Specific Comments 2. Figure 2b, there are large uncertainties for the PBLH height. How would that affect the correlation between PBLH and $PM_{2.5}$ concentrations?

Response: We would like to clarify that the error bars in Fig. 2b represent the standard deviation of the monthly PBLH, not the instantaneous retrieval uncertainty. This standard deviation quantifies the substantial natural variability of PBLH within a given month, arising from both diurnal cycles and day-to-day synoptic changes.

The presence of these significant standard deviations is, in fact, expected and underscores the dynamic nature of the PBLH. The key point is that despite these substantial standard deviations, the monthly average PBLH exhibits a clear and robust seasonal progression (e.g., low PBLH in winter, high PBLH in summer). The anti-correlation we observe with monthly $PM_{2.5}$ emerges precisely because the dominant seasonal forcing synchronizes the behavior of both variables. In other words, the seasonal signal is strong enough to be clearly discernible above the noise of the intra-monthly fluctuations. Therefore, we are confident that the reported anti-correlation is a statistically robust feature reflecting the coupled seasonal evolution of $PM_{2.5}$ and PBLH.

Specific Comments 3. Figure 4, the mass fraction of a certain component would be affected by the concentrations of other components. What would be the corresponding results for the correlation for absolute mass concentrations?

Response: We thank the reviewer for raising this important question. Following the suggestion, we conducted additional correlation analyses using absolute mass concentrations. The results offer more nuanced insights that complement and strengthen our original interpretation based on mass fractions.

The weak correlation between the mass concentrations of SOA/sulfate and PBLH in Fig. R11b below indicates that the dilution effect caused by higher PBLH is nearly offset by their enhanced photochemical production under conditions of high solar radiation and temperature, which aligns with the conclusions in the manuscript. In contrast, the mass fractions of SOA and sulfate show clearer positive correlations with both PBLH and T (Fig. R12). This suggests that although their mass concentrations may not change dramatically, their relative contribution to $PM_{2.5}$ becomes more dominant when other components—particularly nitrate—decrease under higher PBLH and T conditions. Thus, the mass fraction more sensitively captures their role as major components during clean, photochemically active periods.

Nitrate exhibits strongly consistent negative correlations with both PBLH and T in terms of both mass concentration and mass fraction (Fig. R11 and R12). This coherence confirms that its mass concentration is highly sensitive to meteorological conditions, with low T and low PBLH promoting rapid accumulation and formation.

In summary, the comparison between mass concentrations and mass fractions correlations is not contradictory but complementary. It robustly supports our central thesis regarding the differential responses of chemical components. Ultimately, we focused the main-text figure on mass fractions because this representation most clearly isolates and visualizes the differential sensitivity of the components by normalizing for total $PM_{2.5}$ variability.

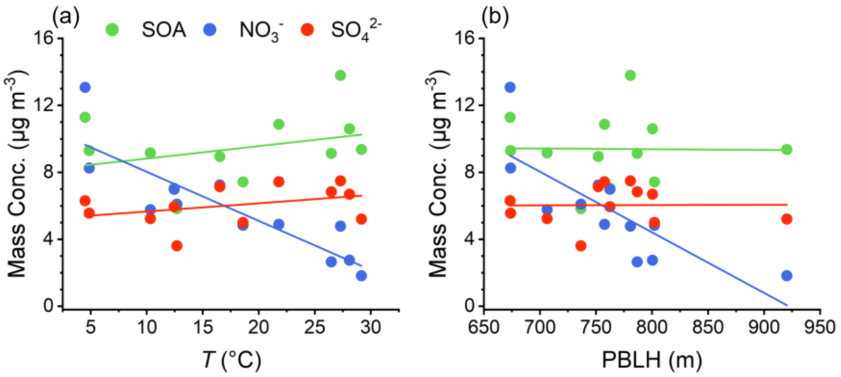

Figure R12: The correlation and linear fitting lines between the monthly average mass concentrations of SOA, sulfate, nitrate and the corresponding monthly average (a) *T* and (b) PBLH.

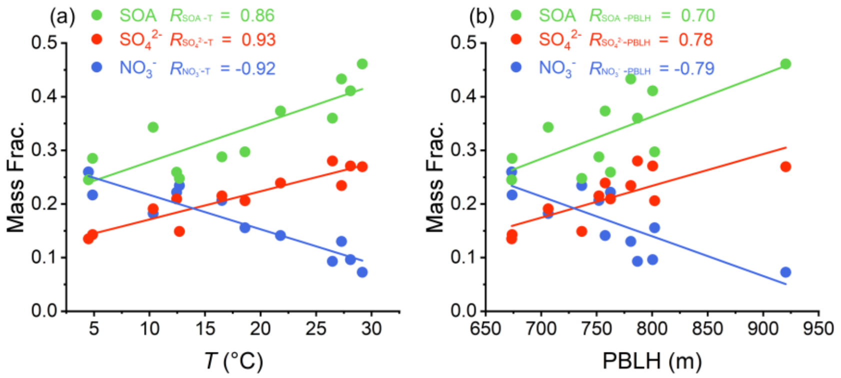

Figure R13: The correlation and linear fitting lines between the monthly average mass fractions of SOA, sulfate, nitrate in PM$_{2.5}$ and the corresponding monthly average (a) *T* and (b) PBLH. *R*SOA-T, *R*SO$_4^{2-}$-T, *R*NO$_3^-$-T: correlation coefficients with *T*. *R*SOA-PBLH, *R*SO$_4^{2-}$-PBLH, *R*NO$_3^-$-PBLH: correlation coefficients with PBLH.

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