## Response to Reviewer # 1

We appreciate the anonymous reviewer for the thoughtful reviews and comments. We have carefully considered the suggestions and revised the manuscript accordingly. The reviewer comments are in blue, our comments are in black, and modifications to the manuscript are in red.

General comments:

Kim et al. have substantially improved the manuscript, and the dataset is valuable. However, several structural, interpretive, and technical issues remain that should be addressed before acceptance in Atmospheric Chemistry and Physics. Below I list Major (structural/scientific) items followed by Specific & Technical (line- or figure-level) points.

We sincerely thank the Editor for the thoughtful and constructive feedback on our manuscript. We also appreciate the reviewers' supportive comments recommending acceptance. In response to the Editor's request for structural and narrative improvements, we have carefully revised the manuscript to enhance clarity, flow, and conciseness while maintaining the scientific depth.

Major revisions include:
(1) Complete reorganization of Section 3.1 to follow Overview → SOA → POA → NOA*;*
(2) Clearer explanation of how the NOA factor was identified and why it emerged in this study;
(3) Reordering and refinement of Section 3.3.1 with a focus on results and evidence-based interpretation; and
(4) Rewriting of the Conclusion to emphasize the two principal findings (NOA and volatile MO-OOA).

We also performed comprehensive copy-editing and addressed all figure-level and line-level comments. Details are provided below.

Major comments

1. Restructure Section 3.1 (clarity and reader flow).

Because resolving NOA is central to the manuscript and many readers may be unfamiliar with this factor, I recommend reorganizing Section 3.1 as: Overview → SOA → POA → NOA. This order (from broadly known to newly resolved) will help readers understand the factors that are consistent with previous studies before introducing the novel NOA factor. As NOA is closely related to POA, discuss NOA immediately after POA.

We appreciate this valuable suggestion. Section 3.1 has been completely reorganized to follow the requested sequence, improving the narrative flow and reader comprehension. The section now begins with a short overview of total $PM_1$ composition, followed by SOA, POA, and finally NOA.

**Revised text (excerpt):**

"Among the organic aerosols, six OA factors were identified during the winter of 2019: hydrocarbon-like OA (HOA; 14%; O:C = 0.13), cooking-related OA (COA; 21%; O:C = 0.18), nitrogen-enriched OA (NOA; 2%; O:C = 0.22), biomass burning OA (BBOA; 13%; O:C = 0.25), and two types of secondary organic aerosols—less-oxidized oxygenated OA (LO-OOA; 30%; O:C = 0.68) and more-oxidized oxygenated OA (MO-OOA; 20%; O:C = 1.15) (Fig. 1e and Fig. S2). These compositions are consistent with previous wintertime observations in Kim et al. (2017), with the exception of newly resolved NOA source. In the following sections, we describe each OA factor in the order of secondary OA (SOA), primary OA (POA) and finally introduce NOA, which—while related to combustion POA—emerged as a distinct, nitrogen-rich factor under the winter conditions of this study~."

2. Clarify how NOA was identified and why it appears now.

In Section 3.1.1, first explain the diagnostics that establish the NOA factor (spectral markers, HR signatures, diurnal behavior, correlations). After that, discuss why NOA was resolved during this campaign but not in prior campaigns in Seoul (e.g., instrumental mode/resolution differences, episodic source enhancement, seasonality, PMF settings). And lastly, compare NOA characteristics with observations in other cities to contextualize uniqueness vs. commonality.

We appreciate this thoughtful and constructive suggestion. The original manuscript included several elements of the NOA diagnosis and inter-campaign comparison, but these were distributed across sections and not presented in a clear order. In the revised version, Section 3.1.1 has been **substantially reorganized** to follow the structure recommended by the reviewer:

**Revised text (excerpt):**

"The NOA factor was identified based on distinct spectral markers, high-resolution chemical signatures, and diurnal behavior. Chemically, this factor exhibited the highest nitrogen-to-carbon (N:C) ratio (0.22) and the lowest oxygen-to-carbon (O:C) ratio (0.19) among all OA factors (Fig. S2), indicating a chemically reduced, nitrogen-rich composition. The high-resolution mass spectrum was dominated by amine-related fragments, including m/z 30 ($CH_4N^+$), 44 ($C_2H_6N^+$), 58 ($C_3H_8N^+$), and 86 ($C_5H_{12}N^+$) (Fig. 3a). Specifically, the spectral signature is defined by the characteristic dominance of the *m/z* 44 fragment—typically the primary marker for dimethylamine (DMA)-related species—closely followed by *m/z* 58 (trimethylamine, TMA) and *m/z* 30 (methylamine, MA). The presence of non-negligible signals at *m/z* 58 and *m/z* 86 further supports the contribution of slightly larger alkylamines (Ge et al., 2011; Silva et al., 2008).

In terms of temporal behavior, NOA displayed a diurnal pattern similar to that of BBOA, with both peaking at night and in the early morning (Fig. 2a). Strong correlations with amine fragments $CH_4N^+$ (r = 0.95) and $C_2H_6N^+$ (r = 0.91) (Fig. 2) confirm that this factor represents reduced nitrogen compounds. While amines can originate from industrial sources or solvent use (e.g., TEA, DEA) (Tiszenkel et al., 2024; Zheng et al., 2015), the dominance of small alkylamines and the covariation with combustion markers suggest a primarily combustion-linked influence, likely associated with biomass burning or residential heating (Ge et al., 2011; You et al., 2014). However, the time series of NOA and BBOA were not perfectly correlated (Fig. 2 and S7), likely because NOA episodes were preferentially enhanced during stagnant haze periods (Fig. 1), whereas BBOA emissions followed a more regular daily emission pattern.

Although nitrogen-containing species have been identified in Seoul via filter-based analysis (Baek et al., 2022), PMF-based resolution of NOA in real-time has not been reported in prior wintertime studies. The successful isolation of NOA in this study is likely driven by the synergistic effect of stagnation and favorable thermodynamic conditions, which significantly elevated particle-phase concentrations. The detection of NOA is often limited by its low mass concentration and high volatility; however, in this campaign, persistent stagnation caused pollutants to accumulate, frequently elevating NOA concentrations above 1 µg $m^{-3}$ during haze events (Fig.2). Simultaneously, the consistently cold and humid winter conditions ($T = -0.24$ °C; RH ≈ 57%) favored the gas-to-particle partitioning of semi-volatile amines (Fig. S2), ensuring that this accumulated mass remained in the particle phase. This combination of physical accumulation and thermodynamic partitioning improved the signal-to-noise ratio, allowing the HR-ToF-AMS to mathematically distinguish the NOA factor from the bulk organic aerosol—a separation that relies on the instrument's ability to resolve isobaric nitrogen-containing ions from hydrocarbon fragments once concentrations are sufficiently high.

The NOA factor contributed approximately 2% of the total organic aerosol (OA) mass, a fraction comparable to observations in Guangzhou (3%; Chen et al., 2021), Pasadena (5%; Hayes et al., 2013), and New York (5.8%; Sun et al., 2011). The spectral profile identified in Seoul is in strong agreement with NOA factors resolved in these diverse environments. For instance, the dominance of *m/z* 44 and *m/z* 30 aligns with amine factors reported in New York City (Sun et al., 2011) and Pasadena (Hayes et al., 2013). This DMA-dominated signature is also consistent with the seasonal characterization of organic nitrogen in Beijing (Xu et al., 2017) and Po Valley, Italy (Saarikoski et al., 2012). Taken together, these results confirm that the NOA resolved in Seoul shares a common chemical signature with reduced organic nitrogen observed globally, representing semi-volatile species that originate from primary urban combustion but are enhanced in the particle phase by rapid secondary partitioning."

3. Reorder Section 3.3.1 and avoid overreaching language.

Present results first, then discussion. Limit speculative material and ensure that mechanistic claims are supported by measurements or cited modeling. The current Section 3.3.1 contains speculative text that is not directly supported by the manuscript's measurements. Retain the essential discussion (the paragraph that addresses reasons for higher volatility of MO-OOA) but shorten and focus the first paragraph; place tentative hypotheses in the Discussion with clear labeling as speculation.

I recommend avoiding the word "Mechanism" in the subsection title unless direct mechanistic evidence is presented. A more suitable and descriptive title would be something like "High-volatility nature of MO-OOA in Seoul wintertime."

We have restructured Section 3.3.1 to follow a clear results → interpretation → speculation (labeled) format. The subsection title was changed from Mechanism of MO-OOA volatility to High-volatility nature of MO-OOA in Seoul wintertime. The revised section is now concise and evidence-driven, with speculative content explicitly labeled.

**Revised text:**

"MO-OOA exhibited high O:C ratios and high apparent volatility, characteristics that were further amplified during haze episodes—periods marked by reduced ozone levels, low solar radiation, and elevated aerosol mass concentrations (Fig. 6 and Fig. S6, yellow shading). Spectrally, MO-OOA was defined by a consistently high $f_{44}$ ($CO_2^+$) signal and a comparatively stable $f_{43}$ ($C_2H_3O^+$) signal relative to LO-OOA (Fig. S8b). Notably, when MO-OOA concentrations intensified during haze, only $f_{44}$ was significantly enhanced, while $f_{43}$ remained nearly unchanged (Fig. 6). This trend is corroborated by the haze–non-haze comparison (Fig. S12), where haze periods (including high MO-OOA intervals) showed elevated contributions from oxygenated fragments (*m/z* 28, 29, 44) and higher O:C ratios. In contrast, non-haze periods were characterized by larger fractional contributions from hydrocarbon-like fragments (*m/z* 41, 43, 55, 57). The observed temporal pattern—elevated $f_{44}$ without corresponding changes in $f_{43}$—is a typical signature of highly oxidized and fragmented organic aerosol, suggesting that aging was dominated by fragmentation rather than functionalization (Kroll et al., 2009). These spectral patterns collectively indicate that MO-OOA is highly oxidized yet remains relatively volatile compared to LO-OOA.

The elevated volatility of MO-OOA despite its high O:C (~1.15) indicates that oxidation under these haze conditions did not follow the classical multi-generational OH-driven aging pathway, which typically increases molecular mass and reduces volatility. Instead, the data align with fragmentation-dominated aging, where highly oxygenated but lower-molecular-weight compounds (e.g., small acids or diacids) are formed. Prior field and laboratory studies using online AMS/FIGAERO-CIMS and EESI-TOF have similarly reported high-O:C yet volatile product distributions characterized by high $f_{44}$ and stable $f_{43}$ (Kroll et al., 2009; Ng et al., 2010; Chhabra et al., 2011; Lambe et al., 2012; Lopez-Hilfiker et al., 2016; D'Ambro et al., 2017).

While direct mechanistic measurements were not available in this study, we hypothesize that the formation of this volatile, high-O:C component may be driven by specific low-light oxidation pathways consistent with the observed environmental conditions. The suppressed ozone levels during haze likely indicate a low-OH oxidation regime (Fig. 6). Under such conditions, radical chemistry involving $NO_3$ (which is longer-lived in low light) or particle-phase autoxidation could preferentially produce highly oxygenated but relatively small organic fragments (Ehn et al., 2014; Zhao et al., 2023). Although haze suppresses photolysis, HONO concentrations—maintained via heterogeneous conversion or surface emissions—could still provide a non-negligible source of OH (Gil et al., 2021; Kim et al., 2024; Slater et al., 2020). Furthermore, the high aerosol mass loadings during haze ($C_{oa}$) provide abundant surface area for absorptive partitioning (Pankow, 1994; Donahue et al., 2006). This increased partitioning mass allows even relatively volatile, oxidized compounds to condense into the particle phase, contributing to the high apparent volatility and oxidation state observed (Jimenez et al., 2009; Ng et al., 2016). Consequently, these results underscore the need for SOA models to incorporate fragmentation-dominated pathways to accurately represent wintertime haze evolution."

4. Revise the Conclusion to emphasize NOA and the volatile MO-OOA observation.

The first paragraph of the Conclusion currently omits a balanced discussion of NOA's mixed primary/secondary nature and overemphasizes biomass burning. Combine the first two paragraphs and use that space to emphasize the manuscript's principal takeaways: (a) reliable identification of a NOA factor and its mixed origin, and (b) the observation that MO-OOA in Seoul exhibits unexpectedly high volatility. Frame outstanding uncertainties and recommended follow-up analyses/measurements as clear next steps.

We agree and have rewritten the Conclusion to highlight these two main contributions and add concise statements on implications and next steps.

**Revised text:**

"This study provides a comprehensive characterization of wintertime submicron aerosols ($PM_1$) in Seoul, integrating chemical composition, volatility measurements, and source apportionment to reveal critical insights into urban OA evolution. The two most significant findings are the robust real-time identification of a nitrogen-containing organic aerosol (NOA) factor and the observation of unexpected volatility behavior in highly oxidized OA. The NOA factor, spectrally dominated by low-molecular-weight alkylamine fragments, was successfully resolved primarily due to the accumulation of pollutants during wintertime stagnation, which sufficiently enhanced the spectral signals of these semi-volatile species for identification. Its temporal and chemical characteristics point to a mixed primary/secondary origin: driven by direct combustion emissions (e.g., residential heating) but significantly enhanced by the rapid gas-to-particle partitioning of semi-volatile amines under cold, humid conditions. Concurrently, the volatility analysis revealed a striking decoupling between oxidation state and volatility for the More-Oxidized Oxygenated

OA (MO-OOA). Despite its high O:C ratio (~1.15), MO-OOA exhibited elevated volatility, a deviation from classical aging models that typically associate high oxidation with low volatility. This behavior is attributed to the specific conditions of winter haze—reduced photolysis and high aerosol mass loadings—which favor fragmentation-dominated aging pathways and the absorptive partitioning of volatile oxygenated products.

These results revise our understanding of wintertime aerosol dynamics and underscore the limitations of current models in representing reduced-nitrogen species and non-canonical oxidation pathways. To address the remaining uncertainties, future research should prioritize evaluating the seasonal variability of NOA to better disentangle the influence of meteorological drivers from specific emission sources. Concurrently, there is a critical need to directly probe radical oxidation mechanisms, such as $RO_2$ autoxidation and $NO_3$ chemistry, particularly under haze conditions. Integrating these field inquiries with laboratory studies and advanced molecular-level measurements (e.g., FIGAERO-CIMS, EESI-TOF) will be essential for constraining the formation, lifetime, and climate impacts of these complex organic aerosol components in polluted megacities."

Specific & technical comments (line- and figure-level)

Manuscript-wide editorial/formatting

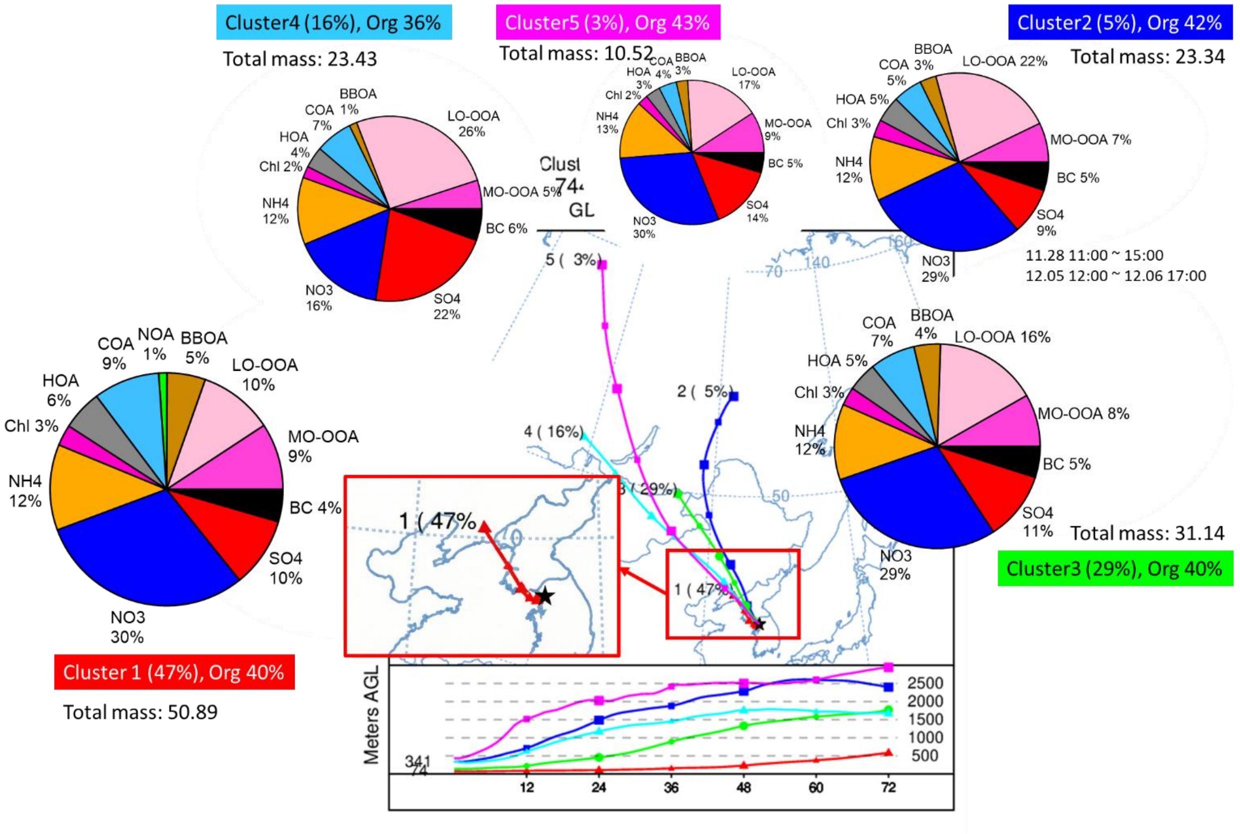
There are numerous minor formatting and grammar issues (missing spaces after punctuation, double punctuation, inconsistent font sizes, inconsistent spacing around "m/z", missing italics for m/z and f##). Please perform a careful copy-edit before the next submission.

We performed a detailed copy-edit to correct punctuation spacing, double punctuation, inconsistent fonts, "m/z" and "f##" formatting, and italicization.

Figures/visualization

Line 186 / Fig. S8: Cluster 1 is not well visualized in Fig. S8. Provide a zoomed-in version (or higher-resolution panel) so the cluster interpretation is clear.

We agree that the resolution of Cluster 1 in the original figure was insufficient. To address this, we have modified Figure S8 to include a zoomed-in inset that clearly displays the trajectory details for this cluster. The revised figure is shown below.



Line 409 / f44 and f43: The high and stable f44 and f43 results are important and should be shown in a main-text figure rather than only in the supplement. If retained in the supplement, clearly reference them in the main text and ensure they are visible in the linked supplement figure.

We appreciate the reviewer's suggestion. We agree that the temporal stability of $f_{44}$ and $f_{43}$ is central to understanding the volatility of MO-OOA. Accordingly, we have moved the key time-series data from the supplement to the main text (Figure 6) to ensure they are prominent and directly accessible alongside the relevant discussion.

PMF/factor robustness

- Line 201: Because the NOA mass fraction is low, please report PMF reproducibility metrics (bootstrap). If bootstrap results exist, include them and summarize whether NOA is reproducibly resolved. If not performed, run bootstrap tests to quantify factor stability.

Thank you for your suggestions. We performed bootstrapping to ensure that the PMF solution is robust and stable. The procedure of bootstrap was updated into method section. Relevant figures are updated at supplementary Table S2 and Figure S13 as follows:

“To ensure the robustness of the 6-factor solution, we calculated uncertainties for each PMF factor using the bootstrap method (100 iterations) with the PET toolkit (v2.05) (EPA, 2014; Xu et al., 2018; Srivastava et al., 2021). This method generates a time series distribution for each factor, providing an average concentration and standard deviation; the uncertainty is defined as the standard deviation divided by the average concentration. As shown in Table S2, the 5-factor solution exhibited the lowest average uncertainty (5.10%). While mathematically stable, this low uncertainty is typical of under-resolved solutions where distinct sources are merged. In the 6-factor solution, the average uncertainty increased slightly to 6.06%, with individual factors ranging from 4.26% (MO-OOA) to 9.36% (BBOA). Despite this marginal increase, all factors in the 6-factor solution remained well within the acceptable range (<10%), confirming that the separation of the additional source did not compromise the solution's statistical stability. In contrast, the 7-factor solution showed signs of instability, with the average uncertainty rising to 7.79% and specific factors exceeding 10% (e.g., Factor 3 at 13.32% and Factor 5 at 11.94%). This degradation suggests the splitting of a factor into non-robust artifacts. Therefore, the 6-factor solution was selected as the optimal choice, offering the best balance of chemical resolution and statistical robustness. The average concentration and 1σ variability for the chosen 6-factor solution are presented in Figure S13"

**Table S2.** Uncertainty in factor concentration for the 5 to 7-factor solution from 100 iterations bootstrap.

| | Factor 1 | Factor 2 | Factor 3 | Factor 4 | Factor 5 | Factor 6 | Factor 7 |
|---|---|---|---|---|---|---|---|
| 5-factor solution | 4.73% | 6.46% | 5.95% | 5.78% | 2.59%- | - | - |
| 6-factor solution | 4.26%<br>(MO-OOA) | 5.23%<br>(LO-OOA) | 9.36%<br>(BBOA) | 6.48%<br>(NOA) | 5.24%<br>(COA) | 5.80%<br>(HOA) | - |
| 7-factor solution | 5.45% | 4.97% | 13.32% | 7.09% | 11.94% | 4.85% | 6.90% |

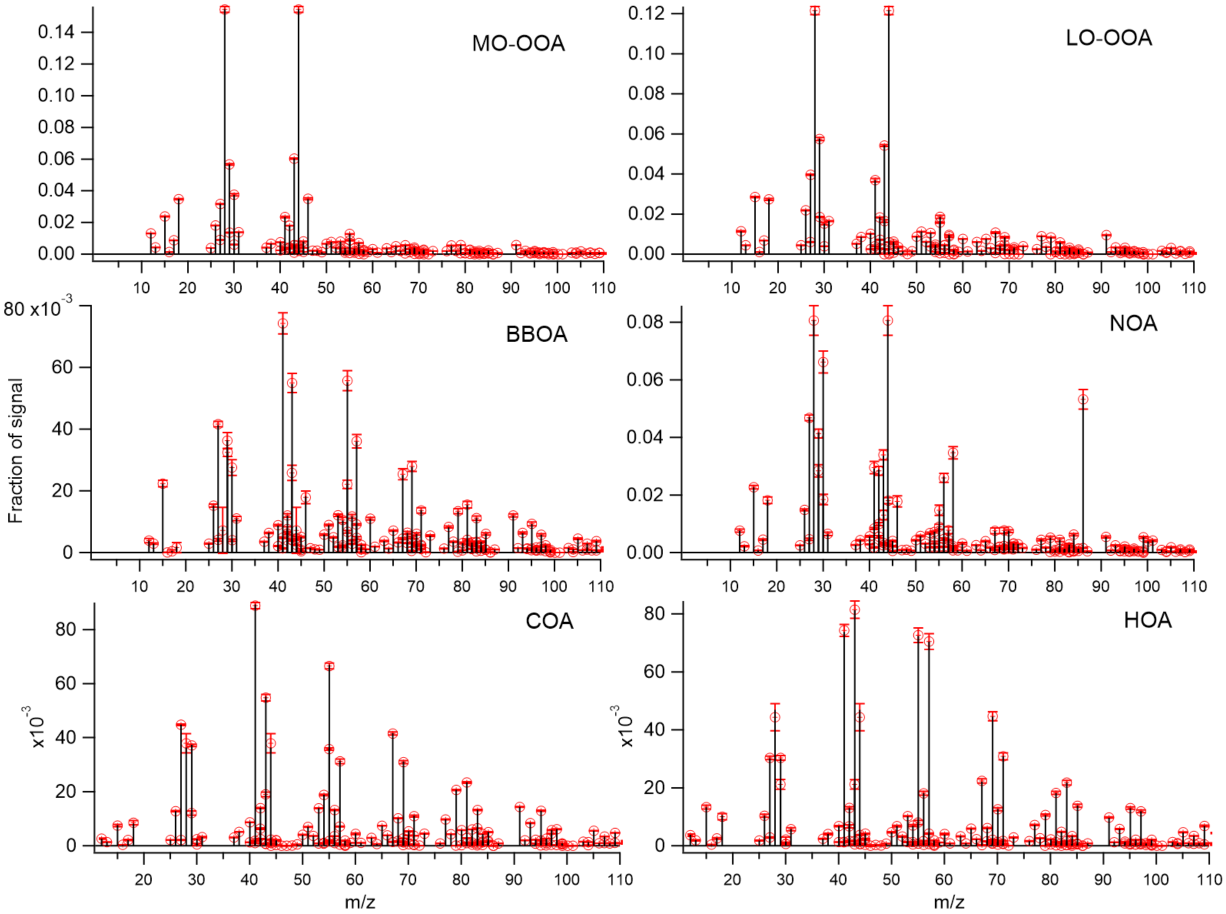


**Figure S13.** Bootstrapping analysis of the 6-factor solution (average factor with 1σ variation for each point)

### Repetition/consolidation

- Lines 208–212 vs. 229–250: These passages appear repetitive (NOA relevance to combustion). Combine and streamline these discussions to avoid redundancy. Place the definitive explanation and supporting evidence in one location.

The repeated passages have been consolidated into a single, concise explanation of NOA's link to combustion in Section 3.1.3.

### Clarifications/wording

Line 257: Clarify "highly oxidized chemical composition." Do you mean "oxidized relative to POA" or "oxidized relative to other OA factors"? Be explicit.

We thank the reviewer for this helpful comment. We have clarified the intended comparison by explicitly stating the reference frame of oxidation. In the revised text, we now specify that the high O:C ratios of MO-OOA (1.15) and LO-OOA (0.68) indicate oxidation levels that are elevated relative to the primary OA factors (HOA, COA, BBOA) and that MO-OOA is substantially more oxidized than LO-OOA. The revised sentence reads:

"The oxygen-to-carbon (O:C) ratios for MO-OOA and LO-OOA were 1.15 and 0.68, respectively, indicating that both factors are highly oxidized relative to the primary OA factors (HOA, COA, BBOA) and that MO-OOA is substantially more oxidized than LO-OOA."

- Line 264: The statement that "LO-OOA is mostly related to primary sources, but not secondary" is ambiguous. Also, wouldn't LO-OOA vs. MO-OOA be more related to "less aged" versus "more aged"?

We thank the reviewer for pointing out this ambiguity and for the insightful suggestion regarding the "aged" distinction. We agree that the terminology "primary vs. secondary" was confusing in this context.

We have revised the manuscript to adopt the reviewer's suggested framework, characterizing LO-OOA and MO-OOA based on their degree of atmospheric processing ("Less Aged" vs. "More Aged") rather than a strict source dichotomy. Our intention is to clarify that while MO-OOA represents highly processed regional aerosol, LO-OOA represents a less aged fraction (fresh SOA) that has not yet undergone the extensive oxidation required to correlate strongly with secondary inorganic species.

"In contrast, LO-OOA exhibited only modest correlations with sulfate, nitrate, and ammonium ($r$ = 0.50, 0.51, and 0.42, respectively). This weaker coupling indicates that LO-OOA represents a less aged oxygenated OA component (fresh SOA), distinguishable from the more aged, highly processed MO-OOA which tracks closely with secondary inorganic species. Regarding potential primary influence, LO-OOA does not exhibit a pronounced *m/z* 60 (levoglucosan) signal (Fig. S2). While the levoglucosan marker ($f_{60}$) is known to diminish with atmospheric aging and can become weak or undetectable downwind (Hennigan et al., 2010; Cubison et al., 2011), the absence of a distinct peak combined with the separation from inorganic salts suggests that LO-OOA is best characterized as freshly formed secondary organic aerosol likely originating from the rapid oxidation of local anthropogenic precursors."

- Line 280: When defining COA, report the m/z 55/57 ratio used as the key tracer for COA identification and show those values or rationale in the text or table.

We appreciate this suggestion. In the revised manuscript, we now explicitly report the *m/z* 55/57 ratio used as a diagnostic for the COA factor and relate it to previous AMS studies to strengthen the identification.

"COA factor showed an enhanced signal at *m/z* 55 relative to *m/z* 57, with a 55/57 ratio of 3.11, substantially larger than that of HOA (1.10). This elevated ratio is consistent with previously reported AMS COA spectra in urban environments (e.g., Allan et al., 2010; Mohr et al., 2012; Sun et al., 2011), supporting our factor assignment."

Line 308: When you state "Nearly complete evaporation occurred by 200 °C (~2% remaining)", indicate explicitly which species you refer to (e.g., nitrate, organics) and include the figure/table reference.

We thank the reviewer for this helpful clarification request. We have revised the text to explicitly state that the ~2% remaining mass refers to the nitrate thermogram and have added the figure reference. Furthermore, we have expanded this section to discuss the $T_{50}$ shift relative to pure ammonium nitrate, clarifying that the residual fraction and the elevated volatilization temperature likely reflect contributions from low-volatility nitrate-containing species (e.g., organonitrates) rather than pure ammonium nitrate.

“Nitrate showed the steepest decline with increasing temperature, with a $T_{50}$ of ~67 °C—substantially higher than that of pure ammonium nitrate (~37 °C; Huffman et al., 2009). At 200 °C, ~2% of the initial nitrate signal remained (Fig. 4). Since pure ammonium nitrate fully evaporates well below this temperature (Huffman et al., 2009), this small residual fraction likely represents the least volatile portion of organic nitrates.”

Lines 311–314: Statements in this range make inferences not directly shown by measurements. Add appropriate references or align the text with the data; avoid speculative assertions without citation.

We thank the reviewer for this helpful comment. We have revised the sulfate thermogram description to remove unsupported inferences and have added appropriate references documenting AMS limitations and sulfate volatility behavior. Specifically, we now clarify that the slope change near 140 °C is consistent with ammonium-sulfate phase transitions or mixed organic–inorganic sulfate interactions reported in previous TD-AMS studies, while explicitly acknowledging that metallic sulfates are not efficiently detected by the AMS.

"Sulfate exhibited the highest thermal stability among the measured species. The thermogram showed a relatively stable mass fraction (MFR > 0.8) up to ~130 °C, followed by a sharp decline at temperatures above 140 °C (Fig. 4). This profile is consistent with the typical volatilization behavior of ammonium sulfate in TD-AMS, which requires higher temperatures to evaporate compared to nitrate or organics (Huffman et al., 2009). At 200 °C, approximately 25% of the sulfate mass remained. This residual suggests the presence of a sulfate fraction with lower volatility than pure ammonium sulfate, likely associated with organosulfates or low-volatility mixtures, whereas refractory metal sulfates are not efficiently detected by the AMS (Canagaratna et al., 2007).”

- Line 318: Specify which chloride species you mean (e.g., ammonium chloride vs. metal chlorides) and provide literature references for volatility comparisons.

Thank you for this important point. We agree that the chloride discussion should be more explicit. We have clarified that the chloride measured by the AMS is expected to be dominated by volatile inorganic chloride, primarily ammonium chloride ($NH_4Cl$), which evaporates efficiently in thermodenuder systems. We have also clarified that metal chlorides (e.g., NaCl, KCl) are far less volatile and are poorly detected by AMS; therefore, they are unlikely to contribute significantly to the observed thermogram.

"Chloride volatility was broadly consistent with prior AMS studies, with $T_{50}$ values comparable across seasons (e.g., Xu et al., 2016; Jeon et al., 2023). The near-complete evaporation observed in winter (~4% residual at 200 °C, Fig. 4) indicates that the chloride measured here was dominated by volatile inorganic chloride, specifically ammonium chloride ($NH_4Cl$), which fully evaporates at relatively low temperatures (Huffman et al., 2009). By contrast, metal chlorides (e.g., NaCl, KCl) are refractory and far less volatile; they are also poorly detected by the AMS (Canagaratna et al., 2007). The lower residual in winter compared to fall (~10%) therefore suggests that wintertime chloride consisted almost exclusively of pure ammonium chloride, whereas the fall samples may have contained a minor fraction of less volatile or refractory chloride species."

Lines 319–321: The current wording is unclear. If you intend to say that organics display a continuous decrease in mass fraction with TD temperature, indicating a range of volatilities, whereas some inorganic species show abrupt loss at specific temperatures, please rewrite explicitly and include references if appropriate.

We thank the reviewer for this helpful clarification request. We agree that the original wording was ambiguous. In the revised manuscript, we explicitly state that the organic thermogram exhibits a smooth and continuous decrease in mass fraction with increasing temperature, reflecting a broad range of volatilities. We now contrast this behavior with the more abrupt, species-specific evaporation transitions typical of inorganic components (e.g., nitrate, ammonium chloride) and have added relevant references.

"Organics exhibited moderate volatility ($T_{50}$ ~120 °C), and their thermogram showed a gradual, continuous decrease in mass fraction with increasing TD temperature. This smooth profile reflects the presence of a broad distribution of organic compounds spanning SVOC to LVOC ranges, in contrast to inorganic species such as nitrate or ammonium chloride, which often show more abrupt losses at characteristic temperatures (Huffman et al., 2009; Xu et al., 2016). This behavior is consistent with previous TD-AMS observations in Seoul during spring and fall (Kang et al., 2022; Jeon et al., 2023)."

Line 334: Oxidation is typically more active during daytime photochemistry. The current statement that tries to explain the higher O:C of HOA is not convincing enough.

We thank the reviewer for this helpful comment. We agree that the previous explanation was imprecise, as oxidation is generally driven by daytime photochemistry rather than nighttime conditions. Our intention was not to imply that these primary factors undergo enhanced atmospheric oxidation at night, but rather to highlight that their O:C ratios are determined by their primary source signatures. BBOA and NOA tend to exhibit slightly higher O:C ratios than HOA because they are emitted with more oxygenated functional groups (e.g., from biomass pyrolysis or amine structures), not because of secondary aging.

To avoid confusion, we have revised the text to remove the misleading reference to photochemistry and provide a clearer, emission-based explanation for the observed O:C differences.

"Among the primary OA (POA) sources, hydrocarbon-like OA (HOA) exhibited the highest volatility, with mass predominantly distributed in the SVOC and IVOC ranges, consistent with its chemically reduced nature (O:C = 0.13) and direct combustion origin. Mass fraction remaining (MFR) results (Fig. S9) further support this, showing rapid mass loss at lower temperatures. Biomass burning OA (BBOA) and nitrogen-containing OA (NOA) also showed high volatility, peaking in the SVOC–IVOC range (log $C^*$ = 1–3), but displayed slightly higher O:C ratios (0.25 and 0.19, respectively). This modest enhancement in O:C reflects their source composition—biomass combustion produces partially oxygenated organic species (e.g., levoglucosan, phenols), and NOA contains nitrogen-bearing functional groups—rather than enhanced atmospheric oxidation."

Line 337: COA appears to be less oxidized than BBOA but also less volatile — please comment on this apparent discrepancy and add discussion.

We thank the reviewer for this insightful comment. We agree that COA displays a distinct volatility-oxidation relationship compared to other primary factors. We have revised the text to clarify that this behavior is consistent with previous TD-AMS studies, which attribute the lower volatility of COA to its specific molecular composition.

"Cooking-related OA (COA) showed a more moderate volatility profile, with mass more evenly distributed across the LVOC and SVOC bins. This behavior differs from that of BBOA, which is slightly more oxidized yet more volatile. This apparent decoupling between oxidation state and volatility is a characteristic feature of COA reported in previous volatility studies (Paciga et al., 2016; Kang et al., 2022). These studies attribute the lower volatility of COA to its abundance of high-molecular-weight fatty acids (e.g., oleic, palmitic, and stearic acids) and glycerides (Mohr et al., 2009; He et al., 2010). Unlike the smaller, fragmented molecules typical of biomass burning, these lipid-like compounds possess high molar masses that suppress volatility, even though their long alkyl chains result in low O:C ratios."

Lines 353–357: These sentences are repetitive. Condense to improve readability.

We thank the reviewer for this suggestion. We have condensed the text to avoid redundancy while retaining the physical explanation for the observed relationship.

"This relationship arises because oxidative functionalization introduces polar groups (e.g., hydroxyl, carboxyl) that increase molecular weight and enhance intermolecular hydrogen bonding, thereby reducing the effective saturation concentration (C*) and promoting particle-phase retention (Jimenez et al., 2009; Kroll and Seinfeld, 2008; Donahue et al., 2011)."

Line 368: Clarify the phrase "strong overall OA volatility" — do you mean "higher volatility" or "greater mass loss upon heating"? Use precise language.

We appreciate the reviewer's comment. The original wording repeated similar ideas about high OA volatility across different cities and seasons, making the sentence longer than necessary. We have condensed this part to present the comparison more efficiently while retaining the essential context from previous TD-AMS studies.

"prior TD-AMS studies in Mexico City, Los Angeles, Beijing, and Shenzhen have all reported substantial SVOC–IVOC contributions during polluted periods, indicating that high OA volatility is a common feature of urban environments across seasons (Cappa and Jimenez, 2010; Xu et al., 2019; Cao et al., 2018)."

Other

- Line 418–421: Material here reads like a summary and is more appropriate for the Conclusion. Consider moving it there.

We thank the reviewer for pointing out that the material in Lines 418–421 previously read as summary-type content. In the revised manuscript, this text has been removed from Section 3.3.1 and incorporated into the Conclusion, consistent with the reviewer's recommendation. The final version of Section 3.3.1 now contains only measurement-based results and focused interpretation, without summary elements.