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. investigated the characteristics of organic aerosol (OA) in Seoul during wintertime haze events. In contrast to previous studies conducted in the region, this work successfully identified a nitrogen-containing OA (NOA) factor, likely associated with biomass burning, in addition to five other OA factors using positive matrix factorization (PMF). A notable finding was that the oxidation state of oxygenated OA (OOA) did not align with volatility: the less-oxidized OOA (LO-OOA) was found to be less volatile than the more-oxidized OOA (MO-OOA). This observation challenges the conventional classification of OOA as semi-volatile or low-volatile and supports the use of LO-OOA and MO-OOA terminology.

The study provides insights relevant to understanding air quality in Seoul, one of the world's largest metropolitan areas, where haze events are increasingly linked to nitrogen-related pollutants. Although NOA contributed only a minor fraction of total OA, its enhancement offers clues about particle-phase chemistry that may worsen air quality and could inform the design of mitigation strategies. Furthermore, this study represents the first attempt in Seoul to connect the oxidation state of OA with volatility, adding useful information to the literature.

However, many of the findings presented are not conceptually new within the broader atmospheric chemistry field. In addition, several interpretations remain speculative, with limited supporting evidence. In particular, Section 3.3 does not convincingly explain why MO-OOA in Seoul appears more volatile than LO-OOA. For these reasons, the work may be more appropriate for publication as a Measurement Report in its current form, unless the discussion and interpretation are substantially strengthened.

Thank you for the thoughtful assessment and for recognizing the potential of our study. We appreciate the concern that some interpretations initially appeared speculative. Guided by your comments, we have substantially strengthened Section 3.3 and clarified several points across the manuscript. We believe the revised paper now goes beyond a measurement-only contribution and meets the criteria for a research article in ACP. In addition to reporting winter measurements, the revision explains the chemistry, evaluates alternative explanations, and situates Seoul in comparison with other major cities—consistent with ACP research-article standards rather than a Measurement Report. We believe these advances are appropriate for a research article in ACP.

Additional comments are provided below.

Major comments:

Section 3.2: This study is presented as a characterization of wintertime aerosol, yet comparisons are made with fall data. Please clarify the source of the fall dataset—was it obtained from your previous work or from another published study? If it is adopted, this needs to be explicitly stated earlier in the section and consistently noted throughout the manuscript, including in figure captions.

Thank you for the comment. Section 3.2 analyzes **only** the winter-2019 dataset collected in this study. To avoid ambiguity, we clarified the phrasing at the few places where this could be misread.

1. **Line 258 :**"Compared to fall (T_{50} ~73 °C, incomplete evaporation), winter nitrate appeared more volatile, supporting enhanced NOA detection and indicating relatively fewer non-volatile nitrate forms."**After:** "Compared to **previously reported fall conditions** (T_{50} ~73 °C, incomplete

evaporation), winter nitrate appeared more volatile, supporting enhanced NOA detection and indicating relatively fewer non-volatile nitrate forms (e.g., Kang et al., 2022; Jeon et al., 2023)."

2. **Line 266:** "Residual ammonium at 200 °C was consistent (~4%) across seasons (Kang et al., 2022; Jeon et al.,2023)." **After:** "Residual ammonium at 200 °C was consistent (~4%) in previously reported spring/fall measurements (Kang et al., 2022; Jeon et al., 2023)."
3. **Line 268:** "Chloride volatility was also comparable between seasons in terms of T_{50}, but exhibited more complete evaporation in winter (~4% residual vs. ~10% in fall), possibly reflecting a shift in source to more volatile forms like road salt during wintertime."**After:** "Chloride volatility was also comparable across seasons in prior studies in terms of T_{50}, but exhibited more complete evaporation in winter (~4% residual vs. ~10% in fall), possibly reflecting a shift in source to more volatile forms like road salt during wintertime."
4. **Line 274**: "This trend aligns with spring and fall observations (Kang et al., 2022; Jeon et al., 2023)."**After:** "This trend aligns with previously reported spring and fall observations (Kang et al., 2022; Jeon et al., 2023)."
5. **Line 292:** "This pattern reflects its diverse cooking sources and variable emission profiles (Kang et al., 2022)."**After:** "This pattern reflects its diverse cooking sources and variable emission profiles as previously reported (Kang et al., 2022)."
6. **Figure 4 caption :"**Mass fraction remaining (MFR) of non-refractory (NR) aerosol species measured in Seoul using a thermodenuder coupled to a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS). Winter 2019 (this study; dashed) is compared with fall 2019 (previously reported; solid) (Jeon et al., 2023).Species include organics (magenta), nitrate (blue), sulfate (orange), ammonium (green), and chloride (red).

Section 3.3: The discussion in this section could be substantially strengthened. For instance, the relatively high volatility of MO-OOA may represent a distinct feature of Seoul compared to other megacities. A more thorough comparison with results from other TD-AMS studies would help contextualize your findings. Given that one of the stated objectives of this work is to "improve understanding of wintertime OA in Seoul," highlighting how Seoul's OOA differs from or aligns with other urban environments would significantly enhance the discussion.

Thank you. Per your suggestion we've strengthened section 3.3 with explicit TD-AMS comparisons to other megacities in the discussion of section 3.3. The updated paragraph (below) now cites representative studies from Mexico City/Los Angeles, Paris, Beijing, and Shenzhen, plus springtime Seoul for seasonal context.

"Viewed against prior TD-AMS results, the volatility of Seoul's winter MO-OOA presents a unique case, particularly in the nature of its O:C-volatility relationship. Prior urban studies have commonly reported substantial SVOC-OA, consistent with high photochemical activity or elevated loadings; for example, Mexico City/Los Angeles showed pronounced SVOC–IVOC contributions during warm seasons (Cappa and Jimenez, 2010), and summertime Beijing and wintertime Shenzhen likewise exhibited strong overall OA volatility (Xu et al., 2019; Cao et al., 2018). While these comparisons establish that volatile OA is common, they generally did not report the factor-level inversion observed here, where the highly-oxidized OOA component (MO-OOA) was *more* volatile than a less-oxidized OOA (LO-OOA). This behavior is distinct from findings in colder, lower-loading regimes; wintertime Paris, for instance, maintained the conventional hierarchy where the more-oxidized OOA was comparatively less volatile (Paciga et al., 2016). Furthermore, seasonal context within Seoul showed springtime OA with lower oxidation levels than our winter MO-OOA despite similar SVOC contributions (Kang et al., 2022). This comprehensive comparison underscores the unusual nature of the O:C-volatility relationship observed under the specific winter haze conditions in Seoul.

Line 163: The claim that enhanced MO-OOA and NOA formation during haze is due to stagnation is not convincing without supporting meteorological data. Please provide wind speed/direction or back-trajectory analyses.

Thank you for this comment. We now document meteorological support for stagnation during haze by (i) presenting back-trajectory clustering that identifies a local recirculation regime (Cluster 1; Fig. S8) and (ii) showing persistently low wind speeds during haze windows in the campaign time series (Fig. S6). These diagnostics indicate that the haze episodes were dominated by local accumulation rather than long-range transport, consistent with the observed co-enhancement of MO-OOA and NOA. Now the relevant section reads;

“Back-trajectory clustering shows frequent short-range recirculation over the Seoul Metropolitan Area during haze (Cluster 1; Fig. S8), and the time series indicates persistently low surface wind speeds during these periods (1.73 ± 0.89 vs. 2.34 ± 1.18 (clean)) (Fig. S6), together pointing to stagnation-driven accumulation of local emissions; the concurrent increases in MO-OOA and NOA are therefore consistent with enhanced in-city formation under stagnant conditions.”

Line 172: Could factor resolution differ between V- and W-mode? Please show whether NOA is detected in both modes and perform PMF sensitivity tests to mode/resolution.

Thank you for the careful question. In the HR-ToF-AMS, W-mode provides higher mass resolving power than V-mode, enabling separation of near-isobaric ions (e.g., *m/z* 58, 86, 100 series) that are important for resolving amine-rich (NOA) spectra; V-mode offers higher sensitivity but lower resolution and is widely used for quantification and bulk metrics, whereas W-mode is preferred for factor analysis of HR ion families. Consistent with standard AMS practice, our PMF was performed on W-mode HR spectra (Methods), where the amine fragments are better separated and uncertainties are well characterized. Running PMF on the lower-resolution V-mode would merge key N-containing ions with interferences and degrade factor identifiability, so we did not perform a V-mode PMF.

Line 194: Since amines can also originate from solvents, might some portion of NOA be linked to solvent emissions? Given Seoul’s solvent usage, this possibility should be addressed.

Thank you for the helpful comment. We agree that solvent- and industry-related amines (e.g., tertiary amines used in polyurethane manufacturing/foams, metalworking, printing, and wastewater treatment) can contribute to urban amine budgets. Reviews and technical sources document such emissions and uses (e.g., TEA/DEEA/DMEA in PU catalysts), and Korean inventories indicate that solvent use is a major component of anthropogenic VOC emissions nationally(references). However, In our dataset, several diagnostics favor near-source combustion/BB influences for NOA during winter in Seoul: (i) night–early-morning peaks and co-variation with BBOA, (ii) back-trajectory clusters indicating local recirculation, and (iii) mass-spectral features dominated by small alkylamine fragments (e.g., *m/z 30*, *44*, *58*, *86*) that match low-molecular-weight alkylamines commonly associated with combustion/BB rather than tertiary amines typical of PU/solvent use. That said, we now explicitly note that a minor contribution from solvent/industrial amines cannot be ruled out, and we added references and a sentence in the Discussion to reflect this possibility.

“These amines are commonly emitted during the combustion of nitrogen-rich biomass and proteinaceous materials and are frequently associated with biomass-burning emissions (Ge et al., 2011). Previous molecular analyses in Seoul also indicate DMA, MA, and TMA as the dominant amine species in December

(Baek et al., 2022). While other amines such as triethylamine (TEA), diethylamine (DEA), and ethylamine (EA) may contribute via industrial/solvent pathways (e.g., chemical manufacturing, petrochemical corridors, wastewater treatment), our HR-AMS spectra are dominated by small alkylamine fragments (*m/z* 30, 44, 58, 86) and the diurnal behavior co-varies with combustion markers (below), indicating a primarily combustion-linked influence. Nevertheless, recent urban measurements and sector-based analyses show that industrial activities can contribute measurable amines in cities (Tiszenkel et al., 2024; Zheng et al., 2015; Mao et al., 2018; Shen et al., 2017; Yao et al., 2016). Accordingly, a minor NOA contribution from solvent/industrial amines cannot be excluded."

Line 199: Where do you expect biomass burning that could influence Seoul's air to occur? Since NOA (linked to BBOA) is a central finding, more discussion on plausible sources and transport pathways would be valuable.

Thank you for this valuable suggestion. We expanded the discussion to identify plausible biomass-burning (BB) source regions and pathways that could influence Seoul and to clarify why our dataset points primarily to local influences. Specifically: (i) wintertime urban/peri-urban small-scale BB (residential solid-fuel use, restaurant charcoal use, and intermittent waste burning) has been observed in Seoul and surroundings (Kim et al., 2017); (ii) agricultural residue burning occurs seasonally in nearby provinces and can episodically affect the Seoul Metropolitan Area (Han et al., 2022); and (iii) regional transport from upwind regions (including northeastern China/North Korea) can influence Korea under northerly/northwesterly flow (Lamb et al., 2018; Nault et al., 2018). In our case, the night–early-morning peaks, co-variation with BBOA, and back-trajectory clusters indicating local recirculation are most consistent with near-source emissions within the metropolitan area during the study period (Yoo et al., 2024). We added further discussion at the end of section 3.1.3.

"Regarding source location, several pathways can influence Seoul's biomass burning signature. First, urban/peri-urban small-scale burning (e.g., solid-fuel use in select households, restaurant charcoal use, and intermittent waste burning) has been reported and can enhance BBOA locally (Kim et al., 2017). Second, nearby agricultural-residue burning in surrounding provinces occurs seasonally and can episodically impact the metropolitan area (Han et al., 2022). Third, regional transport from upwind regions (e.g., northeastern China/North Korea) can bring biomass burning influenced air masses under northerly/northwesterly flow (Lamb et al., 2018; Nault et al., 2018). In this dataset, the nighttime and early-morning enhancements, the BBOA–NOA co-variation, and trajectory clusters showing regional recirculation indicate a predominantly local/near-source contribution during the study period (Yoo et al., 2024), with episodic non-local influences remaining possible."

Line 225: The phrase "…with inorganic secondary species such as biomass burning" is unclear. Please revise.

Thank you for pointing this out. We agree the phrase was ambiguous—biomass burning is a source, not an inorganic secondary species. We removed the confusing wording and clarified the comparison to sulfate, nitrate, and ammonium. Now the relevant line reads:

"In contrast, LO-OOA exhibited only modest correlations with sulfate, nitrate, and ammonium (r = 0.50, 0.51, and 0.42, respectively), suggesting additional contributions from semi-primary sources not closely linked to inorganic secondary formation (e.g., cooking, traffic, biomass burning)."

Line 226: Earlier you noted that LO-OOA lacks m/z 60, but here you attribute it partly to combustion-related activities. This appears contradictory. Please clarify or rewrite.

Thank you for noting the ambiguity. We agree that invoking *m/z 60* (levoglucosan) alongside an earlier statement that LO-OOA lacks *m/z* 60 is confusing. Now the section reads:

"LO-OOA does not exhibit a pronounced m/z 60 (levoglucosan) signal (Fig. S2); however, 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). Taken together, the weaker coupling with secondary inorganics and the absence of a strong m/z 60 peak indicate that LO-OOA is a mixture of aged secondary organics and semi-primary urban emissions, while a contribution from aged biomass-burning influence cannot be ruled out."

Line 257–258: The text seems to imply that NOA could be detected as nitrate. However, most reduced nitrogen species (other than nitro-aromatics, based on Xu et al., 2021, AMT) are unlikely to be detected as nitrate by AMS. Please clarify.

Thank you for pointing this out. We agree that reduced-nitrogen species (e.g., amines) are not detected by the AMS as "nitrate." In the AMS, the nitrate channel reflects inorganic nitrate and organic nitrates ($RONO_2$) via NO^+/NO_2^+ fragments; most reduced-N compounds do not contribute, with the noted exception that nitro-aromatics can appear in the nitrate channel. To avoid confusion, we removed NOA from this sentence and now discuss nitrate volatility independently.

Compared to previously reported fall conditions (T_{50} ~73 °C, incomplete evaporation), winter nitrate appeared more volatile, indicating relatively fewer non-volatile nitrate forms (e.g., Kang et al., 2022; Jeon et al., 2023).

Line 261: If metallic sulfates contribute to PM1, then defining PM1 as NR-PM1 + BC may underestimate total mass. Please comment. Thank you for the helpful comment. Metallic sulfates (e.g., $CaSO_4$, $MgSO_4$, Na_2SO_4) would not be fully captured by the AMS and, if abundant in PM_1, could bias PM_1 = NR-PM_1 + BC low. However, for our winter urban period in Seoul:

1. The HR-ToF-AMS measures non-refractory submicron species; refractory salts typically do not flash-vaporize at the AMS vaporizer and contribute negligibly to the AMS sulfate signal (Allan et al., 2004; Canagaratna et al., 2007).
2. Multiple Seoul/Korea studies show PM_1 is dominated by NR species + BC, with sea-salt/crustal components largely in the coarse mode; our analysis window also excluded dust events, so refractory PM_1 was minimal .
3. The subtle ~140 °C slope change is more plausibly due to ammonium-sulfate system behavior (e.g., morphology/phase-state changes in $(NH_4)_2SO_4$/NH_4HSO_4 and mixed organic–inorganic particles) and/or organosulfate mixing, rather than metallic sulfates (Huffman et al., 2009; Faulhaber et al., 2009).

Accordingly, using PM_1 = NR-PM_1 + BC does not materially underestimate PM_1 for this dataset. We added a sentence in Methods clarifying the non-refractory definition and a note in Results that we interpret the ~140 °C feature as ammonium-sulfate/phase-state and/or organosulfate mixing—not metallic sulfate. Now the relevant section reads;

Line 261:“Sulfate was the least volatile ($T_{50} \approx 170$ °C), consistent with ammonium sulfate (Scott and Cattell, 1979). A subtle slope change near 140 °C likely reflects ammonium-sulfate morphology/phase-state changes and/or organosulfate–inorganic mixing, rather than contributions from metallic (refractory) sulfates, which are not efficiently detected by AMS.”

Methods :“PM_1 mass in this study is taken as NR-PM_1 (from AMS) + black carbon (BC; measured by MAAP), which is appropriate for winter Seoul where refractory PM_1 (metal/sea-salt/crustal) is minor and dust events were excluded (e.g., Kim et al., 2017; Nault et al., 2018; Kang et al., 2022; Jeon et al., 2023).”

Line 289: Since MO-OOA is described as more volatile, the phrase “consistent with its aged, highly condensed nature” seems contradictory. Consider deleting or rephrasing.

Thank you for the suggestion. We deleted the phrase.

Line 308: What alternative oxidation mechanisms or environmental conditions could explain the observed inverse relationship between O:C ratio and volatility? Please specify and cite relevant studies.

Thank you for the comment. We agree the original lead-in was too vague on the mechanisms. We revised the sentence to explicitly foreshadow the explanation that immediately follows (autoxidation-driven fragmentation under low-OH/low-O_3 haze conditions and enhanced condensation at high particle loadings). We also added a section pointer for clarity.

“This observation appears to contradict the usual inverse O:C–volatility relationship; however, under winter haze conditions—with suppressed O_3/low OH, particle-phase autoxidation and fragmentation can yield higher-O:C yet more volatile products, with enhanced condensation on abundant particle surface area (details below).”

Line 311: The authors attribute reduced OH to suppressed O_3 photolysis under haze. However, in polluted boundary-layer conditions, OH production often depends strongly on HONO photolysis in addition to O3 photolysis. If the authors want to keep this statement, I suggest add discussion and relevant reference on this.

Thank you for the comment. We did not measure HONO directly, so our “low-OH” interpretation was based primarily on reduced O_3 photolysis during haze. We now clarify that haze generally reduces actinic flux for *all* photolysis channels, including HONO photolysis, due to aerosol extinction/scattering. At the same time, HONO concentrations often increase at night during polluted, humid conditions because of heterogeneous $NO_2 \rightarrow HONO$ production on surfaces/aerosols and direct/near-surface emissions; thus the net OH from HONO can remain significant or even episodically important despite lower j(HONO). We added text noting both effects and cited field studies in Korea (KORUS-AQ) and China that document (i) reduced photolysis frequencies under haze and (ii) enhanced HONO production via heterogeneous pathways. This balanced perspective does not change our main conclusion (a low-OH regime relative to sunny, high-photolysis periods), but it acknowledges the potential compensating role of HONO under haze.

“We note that haze also suppresses HONO photolysis; however, HONO concentrations can be elevated at night and early morning via heterogeneous NO_2 conversion and surface emissions, so net OH from HONO may remain non-negligible even as photolysis rates are depressed (e.g., Gil et al., 2021; Kim et al., 2024; Slater et al., 2020).

Line 312: Under conditions of reduced OH, how are RO_2 radicals formed and how might they contribute to particle-phase autoxidation? Please elaborate and provide references.

Thank you for the prompt. We clarified that even under reduced OH (low $j(O^1D)$ during haze), RO_2 can arise from (i) residual gas-phase ozonolysis of alkenes (Ehn et al., 2014; Ziemann and Atkinson, 2012; Bianchi et al., 2019), (ii) nighttime/low-light NO_3-initiated chemistry where NO_x and remaining O_3 permit NO_3 formation (Brown and Stutz, 2012; Ziemann and Atkinson, 2012), and (iii) condensed-phase radical chemistry/autoxidation in particles once peroxy radicals are initiated (Kroll and Seinfeld, 2015; Berndt et al., 2016; Bianchi et al., 2019). These routes can sustain RO_2 pools that drive particle-phase autoxidation under haze. Now the line reads;

"Even under low-OH conditions, NO_3 formed via $NO_2 + O_3$ can initiate RO_2 production through addition to alkenes, while reduced photolysis at night/low light extends NO_3 lifetimes; these RO_2 then participate in particle-phase autoxidation, yielding highly oxygenated yet relatively volatile products (Brown and Stutz, 2012; Ziemann and Atkinson, 2012; Ehn et al., 2014; Berndt et al., 2016; Bianchi et al., 2019)."

Line 315–316: To support the interpretation that fragmentation contributes to the high volatility of MO-OOA, please cite previous studies that compared OA composition using both online and offline techniques.

Thank you for the comments. We now cite studies that combine online (AMS/FIGAERO-CIMS) and offline (filter HRMS/GC-MS) techniques showing that fragmentation-dominated aging yields high-O:C yet more volatile products and elevated f_{44} without proportional increases in f_{43}.

"Consistent with this interpretation, online AMS/FIGAERO-CIMS and EESI-TOF, as well as offline HRMS/GC-MS, have reported high-O:C yet more-volatile product distributions accompanied by elevated f_{44} with comparatively stable f_{43} under fragmentation-dominated aging (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)."

Line 317: Please revise "semi-volatile species" to "semi-volatile/intermediate-volatility organics." Additionally, please clearly comment that functionalized but low-molecular-weight compounds can fall in the SVOC–IVOC range and may contribute to the high volatility of MO-OOA. Please provide supporting references.

We revised "semi-volatile species" to "semi-volatile/intermediate-volatility organics (SVOC–IVOC)" and explicitly note that functionalized, low-molecular-weight compounds can fall in the SVOC–IVOC range and thus contribute to the high apparent volatility of MO-OOA. References added.

"Furthermore, high aerosol mass loadings during haze events provide abundant surface area for the uptake of semi-volatile/intermediate-volatility organics (SVOC–IVOC) via absorptive partitioning, so that higher C_{OA} enhances condensation (Pankow, 1994; Donahue et al., 2006; Hallquist et al., 2009; Robinson et al., 2007). We also note that functionalized, low–molecular-weight compounds can reside in the SVOC–IVOC range and thus contribute to the high apparent volatility of MO-OOA (Ng et al., 2010; Chhabra et al., 2011; Lopez-Hilfiker et al., 2016; D'Ambro et al., 2017)."

Line 327–328: A comparison of average OA mass spectra between haze and non-haze periods would be informative. Do non-haze periods show relatively more high-molecular-weight fragments?

Thank you for the insightful comment. We added a direct comparison of average OA mass spectra for haze and non-haze periods (new Fig. S12; events defined in Fig. S6). Because AMS EI at 70 eV produces extensive fragmentation, non-haze periods do **not** exhibit "more high-molecular-weight fragments." The differences are expressed in low-*m/z* markers: haze spectra show enhanced oxygenated fragments (*m/z* 28 = CO^+, 29 = CHO^+, 44 = CO_2^+) together with higher f_{44} and O:C, while f_{43} remains comparatively unchanged. Non-haze spectra display larger fractional contributions of hydrocarbon-like ions (*m/z* 41, 43, 55, 57) and lower f_{44} and O:C. This pattern—increased $\boldsymbol{f_{44}}$ with flat $\boldsymbol{f_{43}}$—is the canonical signature of fragmentation-dominated aging rather than functionalization (Kroll et al., 2009), reinforcing our interpretation that the periods of elevated MO-OOA reflect advanced oxidation and increased volatility arising from autoxidation and the condensation of small oxygenated fragments. Now the sentence reads;

"Consistent with this, the haze–non-haze comparison, including the high-MO-OOA interval (Fig. S12), shows larger oxygenated fragments (m/z 28, 29, 44) and higher f_{44} and O:C during haze, whereas non-haze periods exhibit relatively larger fractional hydrocarbon fragments (m/z 41, 43, 55, 57). These spectral contrasts indicate that the elevated volatility of MO-OOA reflects advanced oxidation—via autoxidation and the condensation of small oxygenated fragments—rather than enrichment of high-molecular-weight ions, particularly under conditions of limited OH and high particulate surface area."

Specific comments:

2 Experimental methods

Line 97: Since you are presenting quantitative results, please specify what collection efficiency (CE) value was applied in the AMS data analysis. In addition, could the use of the thermal denuder (TD) influence CE, for example by altering particle phase state or mixing characteristics? Please clarify whether you assumed the same CE with and without TD and provide justification or relevant references.

Thank you for this point. We apply time-resolved, composition-dependent CE(t) (Middlebrook et al., 2012) separately to the bypass and TD lines. This approach allows CE to vary with the evolving nitrate fraction and neutralization, which TD heating can influence. The campaign-average CE values were TD: 0.55 ± 0.08 and bypass: 0.53 ± 0.04; the mean difference is 0.02 (~3.7%), which is smaller than the combined uncertainty of the two estimates (≈ 0.09). In other words, the CE(t) distributions are similar between lines (comparable means and standard deviations), and we did not force them to be equal—each line's CE(t) was used in its own mass quantification.

We agree that phase-state or mixing changes beyond composition could, in principle, perturb CE. However, prior TD–AMS studies report that such TD-induced CE effects are modest and predominantly multiplicative/near-uniform with respect to thermogram interpretation, not altering thermogram shapes or T_{50} ordering (Huffman et al., 2009; Faulhaber et al., 2009; Cappa & Jimenez, 2010). Given our use of CE(t) that already responds to composition changes, the small TD–bypass CE difference relative to uncertainty, and literature showing minor additional CE impacts from phase/bounce, we consider any residual CE effects beyond composition to be minor for the volatility metrics presented. We have clarified this in the Methods and added the supporting citations.

“NR-PM_1 quantification followed established AMS protocols (Ulbrich et al., 2009; Zhang et al., 2011). Both the bypass and TD streams were processed using a time-resolved, composition-dependent collection efficiency CE(t) following Middlebrook et al. (2012). TD heating can modify particle water and phase state/mixing and thereby influence CE beyond composition (Huffman et al., 2009), but prior TD–AMS studies indicate that such effects are modest and largely multiplicativ**e**, which do not distort thermogram shapes or T_{50} ordering (Faulhaber et al., 2009; Cappa & Jimenez, 2010). In our data, the CE(t) statistics for the two lines were similar (campaign-average CE: TD = 0.55 ± 0.08; bypass = 0.53 ± 0.04; Δ = 0.02 ≈ 3.7%, below the combined uncertainty ≈ 0.09). We therefore report volatility metrics with these line-specific CE(t) corrections applied and interpret potential residual CE effects as minor.”

Finally, if you define PM_1 mass as NR-PM + BC, it would be important to cite studies demonstrating that PM_1 in Seoul contains only limited amounts of metals or other refractory components (e.g., dust, sea salt), otherwise this definition may underestimate the total PM_1 mass.

Thank you for raising this point. In Seoul, multiple ambient studies indicate that submicron mass (PM_1) is dominated by non-refractory species (organics, sulfate, nitrate, ammonium) plus BC, with refractory metal,dust and sea salt contributing only a small fraction to PM_1 (and mainly affecting supermicron/coarse modes). Our study period excludes dust events. Accordingly, defining PM_1 = NR-PM_1 + BC is consistent with prior Seoul observations and with regional aircraft/surface measurements during KORUS-AQ. We have added the following references and a brief note in Methods to clarify this assumption.

“PM_1 mass in this study is taken as NR-PM_1 (from AMS) + black carbon (BC; measured by MAAP), which is appropriate for winter Seoul where refractory PM_1 (metal/sea-salt/crustal) is minor and dust events were excluded (e.g., Kim et al., 2017; Nault et al., 2018; Kang et al., 2022; Jeon et al., 2023)..”

3 Results and discussion

Line 149: Please clarify why a PM level of ~28 μg m^{-3} is considered “moderate.” A reference or comparison to regional air quality standards would help.

Thank you for the suggestion. We now justify “moderate” using (i) prior winter PM_1 in Seoul (27.5 μg m^{-3} on average; stagnant episodes ≈ 44 μg m^{-3}), showing our mean (27.8 ± 15.3 μg m^{-3}) is comparable to the historical winter mean and below stagnant loads, and (ii) a Korea-specific $PM_1/PM_{2.5} \approx 0.8$, which implies an equivalent $PM_{2.5} \approx 34.8$ μg m^{-3}, near the national 24-h $PM_{2.5}$ standard (35 μg m^{-3}). We have added these references and clarifications.

“We conducted continuous measurements from 28 November to 28 December 2019, characterizing a winter period with a mean PM1 concentration of 27.8±15.3μgm−3. This concentration is characterized as moderate; it closely matches historical winter PM1 means in Seoul (Kim et al., 2017) and implies an equivalent PM2.5 concentration is about 34.8μgm−3 (using a Korea-specific PM1/PM2.5≈0.8 (Kwon et al., 2023), which is near the national 24-h PM2.5 standard (35μgm−3) (AirKorea).”

Line 186: A reference regarding the atmospheric lifetime and reactivity of amines would strengthen this discussion.

Thank you for the helpful suggestion. We added citations documenting the short atmospheric lifetimes and high reactivity of alkyl amines due to fast gas-phase oxidation .

"Back-trajectory analysis linked these events to regional recirculation patterns (Cluster 1, Fig. S7), suggesting a predominantly local origin—consistent with the short atmospheric lifetimes and high reactivity of most amines (Ge et al., 2011; Nielsen et al., 2012; You et al., 2014; Hanson et al., 2011). "

Line 242: Please italicize all "m/z ##" and "f##" notations throughout the manuscript for consistency.

Thank you for pointing this out. We have applied consistent typography throughout the manuscript by italicizing all *m/z* and *f* notations (e.g., *m/z* 44, *f*44). This change has been implemented across the main text, figure and table captions, and the Supplementary Information to ensure uniform style.

Line 246: Instead of describing the correlation between NOA and BBOA as "moderate," please quantify the correlation coefficient and state whether it is higher relative to other factor pairs.

Thank you for the suggestion. We replaced the qualitative phrase "moderate" with quantitative values and clarified the context relative to other factor pairs. Specifically, the BBOA–NOA time-series correlation is r = 0.30 (the highest among the NOA–factor pairs examined), and their diurnal-profile correlation is r = 0.63. We retain the ion-level correlations for completeness.

"Quantitatively, BBOA and NOA correlate with r = 0.30 in the time series—the highest among the NOA–factor pairs in our dataset—and their diurnal profiles are more strongly correlated (r = 0.63). Consistent with this, nitrogen-containing ions characteristic of NOA, $C_2H_4N^+$ (r = 0.67) and $C_2H_6N^+$ (r = 0.56), co-vary with BBOA and are dominant peaks in the NOA mass spectrum (Fig. 2; Fig. S3; Fig. S10; Fig. S11)."

Line 248: The phrase "such as biomass burning" may be redundant here, since this point is already discussed in the BBOA section. Consider removing it.

Thank you for the suggestion. We agree that "such as biomass burning" is redundant given the discussion in the BBOA section. We have removed the phrase and streamlined the sentence for clarity. The sentence now reads:

"This overlap suggests a potential shared emission source or co-emission scenario, consistent with the co-emission of both organic aerosols and reduced nitrogen-containing compounds"

Line 300–303: Please provide supporting references for this discussion.

We added references demonstrating that functionalization typically lowers volatility, while fragmentation increases it and can reduce SOA yields despite higher O:C; this supports our emphasis on pairing composition with direct volatility constraints. Now the section reads;

"the addition of oxygen-containing functional groups (e.g., hydroxyl, carboxyl, carbonyl) increases molecular weight and enhances intermolecular interactions such as hydrogen bonding, thereby reducing vapor pressure (Jimenez et al., 2009; Kroll and Seinfeld, 2008). Moreover, oxidative aging often leads to oligomerization or functionalization, promoting particle-phase retention and reducing the effective saturation concentration (C∗) (Donahue et al., 2011; Robinson et al., 2207).”

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