Response to Reviewer # 2

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.

Kim et al. present a study of aerosol chemistry during wintertime in Seoul in 2019. Building upon their earlier publication in 2017, the authors conducted a dedicated field campaign focusing on aerosol volatility and obtained several intriguing results that are highly relevant to understanding and modeling aerosol processes in this megacity. One particularly interesting finding is that highly oxidized organic aerosols were shown to be highly volatile, providing observational evidence for autoxidation and fragmentation processes occurring in the particle phase. The dataset is well analyzed, and the manuscript is clearly written. The study fits well within the scope of ACP, and I consider it suitable for publication as a research article, rather than a measurement.

We appreciate the thoughtful reviews and comments. We appreciate the recognition that our findings, particularly the observational evidence for autoxidation and fragmentation leading to highly oxidized but volatile organic aerosols, are highly relevant to understanding and modeling aerosol processes in the region. 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.

Section Introduction: The Introduction could be further strengthened by expanding the background on aerosol volatility. Including more context on previous volatility-related studies would help frame the contribution of this work.

Thank you for this helpful suggestion. To clarify the aims and frame our contribution, we expanded the Introduction to explain why OA volatility is central to gas–particle partitioning and model performance, and summarize frameworks that couple volatility and oxidation. These changes/additions help motivate our TD-AMS approach and the winter focus of this study. Now the relevant section reads:

"Volatility is a key parameter for characterizing organic aerosol (OA) properties, as it governs gas-to-particle partitioning behavior and directly influences particle formation yields (Sinha et al., 2023). The classification of OA species based on their volatility—from extremely low-volatility (ELVOC) to semi-volatile (SVOC) and intermediate-volatility (IVOC) compounds—is central to the conceptual framework of secondary OA (SOA) formation and growth (Donahue et al., 2006). It also affects atmospheric lifetimes and human exposure by determining how long aerosols remain suspended in the atmosphere (Glasius and Goldstein, 2016). Therefore, accurately capturing OA volatility is essential for improving predictions of OA concentrations and their environmental and health impacts. However, chemical transport models often significantly underestimate OA mass compared to observations (Matsui et al., 2009; Jiang et al., 2012; Li et al., 2017), largely due to incomplete precursor inventories and simplified treatment of processes affecting OA volatility. For instance, aging—through oxidation reactions such as functionalization and fragmentation—can significantly alter volatility by changing OA chemical structure (Robinson et al., 2007; Zhao et al., 2016). Early volatility studies primarily utilized thermal denuders (TD) coupled with various detection instruments to investigate the thermal properties of bulk OA (Huffman et al., 2008). The subsequent coupling of TD with the Aerosol Mass Spectrometer allowed for component-resolved volatility

measurements, providing critical, quantitative insight into the properties of OA factors (e.g., SV-OOA vs. LV-OOA) across different regions (Paciga et al., 2016; Cappa and Jimenez, 2010). These component-resolved volatility data are often used to constrain the Volatility Basis Set (VBS)—the current state-of-the-art framework for modeling OA partitioning and evolution (Donahue et al., 2006). However, a limitation in many field studies is that the TD-AMS thermogram data are rarely translated into quantitative VBS distributions for individual OA factors, which limits their direct use in chemical transport models. Furthermore, the volatility of OOA during extreme haze conditions, where the expected inverse correlation between oxidation (O:C) and volatility can break down (Jimenez et al., 2009), remains poorly characterized, particularly in East Asia's highly polluted winter environments. A recent study in Korea further highlighted the importance of accounting for such processes when interpreting OA volatility under ambient conditions (Kang et al., 2023). Given its central role in OA formation, reaction, and atmospheric persistence, volatility analysis is critical for bridging the gap between measurements and model performance."

Section 2.1: This section currently begins with a citation to the authors' earlier study, which may lead readers to assume that the dataset is the same. However, the actual description of the 2019 field study only appears several sentences later. To improve clarity and logical flow, I suggest first presenting the details of the current field campaign and then referring back to the earlier study for context.

We appreciate the suggestion. We rewrote the opening of section 2.1 to first describe the 2019 field campaign and site, followed by a brief pointer to our earlier winter study for background on the same location. We believe this improves the logical flow and avoids confusion with the 2017 dataset. Now the relevant section reads;

"We conducted continuous real-time measurements in Seoul, South Korea, from 28 November to 28 December 2019. The sampling site was located in the northeastern part of the city (37.60° N, 127.05° E), approximately 7 km from the city center, surrounded by major roadways and mixed commercial–residential land use. Air samples were collected at an elevation of approximately 60 meters above sea level, on the fifth floor of a building. A detailed site description has been reported previously for winter Seoul (Kim et al., 2017). During this period, the average ambient temperature was 1.76 ± 4.3 °C, and the average relative humidity (RH) was 56.9 ± 17.5%, based on data from the Korea Meteorological Administration (http://www.kma.go.kr)."

Line 146-150: This paragraph relies on information from the Supplementary Material, which makes it awkward as an entry point into the main results. I suggest either removing it or integrating the content later in the manuscript, once the main results are introduced.

Thank you for the helpful suggestion. We agree that starting a section by referencing time series data in the Supplementary Material (Fig. S6) made the initial description awkward. We have reorganized the opening of the Results section (section 3.1).The revised introductory paragraph now immediately establishes the campaign's characteristics, providing the necessary meteorological and concentration context before detailing the composition in Fig. 1. The revised section now reads:

"We conducted continuous measurements from 28 November to 28 December 2019, characterizing a winter period with a mean PM_1 concentration of **27.8±15.3μgm^{-3}**. This concentration is characterized as moderate; it closely matches historical winter PM_1 means in Seoul (Kim et al., 2017) and implies an equivalent $PM_{2.5}$ concentration is about 34.8μgm^{-3} (using a Korea-specific $PM_1/PM_{2.5}$≈0.8 (Kwon et al., 2023)), which is near the national 24-h $PM_{2.5}$ standard (35μgm^{-3}) (AirKorea). The full co-evolution of PM_1, gaseous pollutants, and meteorological conditions is provided in Fig. S6, showing an average ambient temperature of 1.76±4.3°C and average relative humidity (RH) of 56.9±17.5% during the study.

Figure 1 summarizes the overall non-refractory submicron aerosol (NR-PM1) composition and the identified OA factors.~"

Section 3.1.1: The identification of nitrogen-containing organic aerosols (NOA) could be better supported. I encourage the authors to provide additional evidence, for instance through mass spectral comparison with previous studies, or by applying the NO/NO_2 ratio approach to assess NOA, and then comparing the results with PMF-based identification.

Thank you for the helpful suggestions. We agree that the identification of NOA must be clearly supported. Regarding the NO^+/NO_2^+ ratio: This metric is a well-established diagnostic for assessing the thermal decomposition (and thus functionality) of inorganic or organic nitrate (NO_3^-) in the AMS nitrate channel. It is not applicable to reduced-nitrogen amines ($R{-}NH_2$) that define NOA, which are detected in the organic spectrum as reduced $C_xH_yN^+$ fragments (e.g., m/z30,44,58,86). Accordingly, we did not apply the NO^+/NO_2^+ method to the NOA factor. In order to strengthen the mass spectral evidence as requested, we have enhanced the discussion in 3.1.1 to clearly emphasize the spectral matching of our NOA factor against established literature reference spectra of amines (Fig. 3). Now the relevant section reads;

"The NOA 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 POA factors (Fig. S2), indicating a chemically reduced, nitrogen-rich composition. The factor represents semi-volatile, reduced nitrogen species that originate from primary urban combustion sources but whose observed mass in the particle phase is enhanced by rapid secondary partitioning and salt formation (Ge et al., 2011; You et al., 2014). The NOA 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). The spectral signature of the factor is defined by the characteristic dominance of the *m/z* 44 fragment, which typically serves as the primary marker for dimethylamine (DMA)-related species, closely followed by *m/z* 58 (trimethylamine, TMA) and *m/z* 30 (methylamine, MA). This profile is in strong agreement with NOA factors resolved via PMF in other polluted 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, California (Hayes et al., 2013). This DMA-dominated signature is also consistent with seasonal characterization of organic nitrogen in Beijing (Xu et al., 2017) and Po Valley, Italy (Saarikoski et al., 2012), reinforcing the common chemical signature of reduced organic nitrogen across diverse urban and regional environments. Furthermore, the presence of non-negligible signals at *m/z*58 and *m/z* 86 supports the contribution of slightly larger alkylamines, a pattern that aligns well with established AMS laboratory reference spectra for these reduced nitrogen compounds (Ge et al., 2011; Silva et al., 2008)"

Line 187-188: Please clarify whether the identified NOA is of primary or secondary origin.

Thank you for requesting this clarification. The NOA factor exhibits characteristics of both primary emissions and rapid secondary processing, which is typical for reduced nitrogen species. We have clarified in the manuscript that the factor is best characterized as a semi-volatile component derived primarily from combustion emissions whose particle-phase concentration is enhanced by atmospheric processing.

We base this conclusion on the following evidence.

1. Primary Origin (Precursors): The mass spectrum (Fig. 3) and elemental ratios (O:C=0.19, low oxidation) closely match low-molecular-weight alkylamines (e.g., DMA, TMA), which are primarily emitted during high-temperature combustion of nitrogen-rich fuels (Ge et al., 2011). The night-early morning peaks (Fig. 2) further link it to near-source urban combustion/heating activities.
2. Secondary Enhancement (Observed Mass): The observed high particle-phase concentration is strongly influenced by secondary processes:
    - Partitioning: Amines are semi-volatile and highly basic. Their particle-phase retention (NOA mass) relies on partitioning facilitated by low temperature and reaction with acidic species to form low-volatility aminium salts (a secondary process).
    - Meteorological Dependence: We observed a strong increase in NOA when relative humidity (RH) surpassed 60% (Fig. 2), suggesting that RH-driven partitioning and enhanced formation of aminium salts are critical for its detection (Milic et al., 2016).

We have revised the text to clearly articulate this dual nature, emphasizing that while the precursor is primary, the particle mass is semi-secondary (governed by partitioning).

"The NOA 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 POA factors (Fig. S2), indicating a chemically reduced, nitrogen-rich composition. **The factor represents semi-volatile, reduced nitrogen species that originate from primary urban combustion sources but whose observed mass in the particle phase is enhanced by rapid secondary partitioning and salt formation (Ge et al., 2011; You et al., 2014).** "

Line 212-213: The abbreviations for OOAs have already been introduced earlier.

We removed repeated definitions of OOA and OA.

Line 267: The abbreviation "OA" has also been defined earlier.

We removed repeated definitions of OOA and OA.

Line 268: ... observations at where?

Thank you for pointing this out. We had not explicitly stated the location. The observations were made in **Seoul, Korea**. We have clarified the sentence accordingly.

"This trend aligns with previously reported spring and fall observations in Seoul, Korea (Kang et al., 2022; Jeon et al., 2023)."

Line 292: Section 3.3?

Corrected. Thanks.

Line 302-303: Please add a few references to situate your results in the context of previous literature.

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:

"Generally, the oxygen-to-carbon (O:C) ratio of organic aerosols (OA) is inversely related to their volatility. As O:C increases through aging, the effective saturation concentration (C*) typically decreases, resulting in lower volatility (Donahue et al., 2006; Jimenez et al., 2009). This common relationship arises because the addition of oxygen-containing functional groups (e.g., hydroxyl, carboxyl, carbonyl),which 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., 2007). However, in this study, the most oxidized OA factor—MO-OOA, with a high O:C ratio of 1.15—exhibited unexpectedly high volatility. Its volatility distribution was skewed toward SVOCs and IVOCs (Fig. 5), and its rapid mass loss in MFR thermograms (Fig. S9) further indicated low thermal stability. 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)."

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