Source-Resolved Volatility and Oxidation State Decoupling in Wintertime Organic Aerosols in Seoul

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Abstract.

Organic aerosols (OA) are key components of wintertime urban haze, but the relationship between their oxidation state and volatility—critical for understanding aerosol evolution and improving model predictions—remains poorly constrained. While oxidation–volatility decoupling has been observed in laboratory studies, field-based evidence under real-world conditions is scarce, particularly during severe haze episodes. This study presents a field-based investigation of OA sources and their volatility characteristics in Seoul during a winter haze period, using a thermodenuder coupled with a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS).

Positive matrix factorization resolved six OA factors: hydrocarbon-like OA, cooking, biomass burning, nitrogen-containing OA (NOA), less-oxidized oxygenated OA (LO-OOA), and more-oxidized OOA (MO-OOA). Despite having the highest oxygen-to-carbon ratio (~1.15), MO-OOA exhibited unexpectedly high volatility, indicating a decoupling between oxidation state and volatility. We attribute this to fragmentation-driven aging and autoxidation under stagnant conditions with limited OH exposure. In contrast, LO-OOA showed lower volatility and more typical oxidative behavior.

Additionally, NOA—a rarely resolved factor in wintertime field studies—was prominent during cold, humid, and stagnant conditions and exhibited chemical and volatility features similar to biomass burning OA, suggesting a shared combustion origin and meteorological sensitivity.

These findings provide one of the few field-based demonstrations of oxidation–volatility decoupling in ambient OA and highlight how source-specific properties and meteorology influence OA evolution. The results underscore the need to refine OA representation in chemical transport models, especially under haze conditions.

Keywords: Organic aerosol volatility, HR-ToF-AMS, Thermodenuder, elemental ratios, aging, fragmentation

1 Introduction

Atmospheric aerosols affect both human health and the environment by reducing visibility (Ghim et al., 2005; Zhao et al., 2013) and contributing to cardiovascular and respiratory diseases (Hamanaka et al., 2018; Manisalidis et al., 2020). In addition, aerosols play a significant role in climate change by scattering or absorbing solar radiation and modifying cloud properties (IPCC AR6). Among the various aerosol components—including sulfate, nitrate, ammonium, chloride, crustal materials, and water—organic aerosols (OA) are particularly important to characterize, as they account for 20–90% of submicron particulate matter (Zhang et al., 2007). Identifying OA sources and understanding their behavior are critical for effective air quality management; however, this is particularly challenging due to the vast diversity and dynamic nature of OA compounds, which originate from both natural and anthropogenic sources. Unlike inorganic aerosols, organic aerosols (OAs) evolve continuously through complex atmospheric reactions, influenced by emission sources, meteorological conditions, and aerosol properties (Jimenez et al., 2009; Hallquist et al., 2009; Robinson et al., 2007; Donahue et al., 2006; Ng et al., 2010; Cappa and Jimenez, 2010).

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,

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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.

Traditionally, due to the complexity and variability of OA, the oxygen-to-carbon (O:C) ratio has been used as a proxy for estimating volatility. In general, higher O:C values indicate greater oxidation and lower volatility (Jimenez et al., 2009). Accordingly, many field studies classify oxygenated OA (OOA) into semi-volatile OOA (SV-OOA) and low-volatility OOA (LV-OOA) based on their O:C ratios (Ng et al., 2010; Huang et al., 2010; Mohr et al., 2012). However, this relationship is not always straightforward. Fragmentation during oxidation can increase both O:C and volatility simultaneously, disrupting the expected inverse correlation (Jimenez et al., 2009). In laboratory experiments, yields of highly oxidized SOA have been observed to decrease due to fragmentation (Xu et al., 2014; Grieshop et al., 2009). These findings suggest that while O:C can offer useful insights, it is insufficient alone to represent OA volatility. Direct volatility measurements, especially when paired with chemical composition data, are necessary to improve our understanding of OA sources and aging processes.

In this study, we investigate the sources and volatility characteristics of OA in Seoul during winter. Wintertime OA presents additional challenges due to its high complexity. During winter, emissions from combustion sources such as biomass burning and residential heating significantly increase, contributing large amounts of primary OA (Kim et al., 2017). Meanwhile, low ambient temperatures and reduced photochemical activity affect the formation and evolution of secondary OA (SOA). Frequent haze events further complicate the aerosol properties by extending aging times and increasing particle loadings. These overlapping sources and atmospheric conditions make winter OA particularly difficult to characterize and predict. ~~Seoul, however, comprehensive studies on OA volatility during winter remain limited, despite the season's significance for air quality management.~~ Despite Seoul's significance for air quality management, comprehensive studies on OA volatility during winter remain limited. To address these goals, we conducted real-time, high-resolution measurements using a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) coupled with a thermodenuder (TD). The objectives of this study are to: (1)

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improve the understanding of wintertime OA in Seoul, (2) characterize the volatility of OA associated with different sources, and (3) explore the relationship between OA volatility and chemical composition.

2 Experimental methods

2.1 Sampling Site and Measurement Period

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).

~~Continuous real-time measurements were conducted in Seoul, the capital of South Korea, where a previous study (Kim et al., 2017) was also performed. Detailed descriptions of the measurement site can be found in that reference. Briefly, 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. Air samples were collected at an elevation of approximately 60 meters above sea level, on the fifth floor of a building. The site is situated near major expressways and is surrounded primarily by commercial and residential areas, indicating substantial influence from anthropogenic and primary emission sources (Kim et al., 2017). Measurements were carried out from November 28 to December 28, 2019. 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).~~

2.2 Instrumentation and Measurements

The physico-chemical properties of non-refractory PM_1 (NR-PM_1) species—including sulfate, nitrate, ammonium, chloride, and organics—were measured using an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) (DeCarlo et al., 2006). 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). Data were acquired at 2.5-minute intervals, alternating between V and W modes. The V mode

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provides higher sensitivity but lower resolution, suitable for mass quantification, whereas the W mode offers higher mass resolution but lower sensitivity, used here for OA source apportionment. Simultaneously, black carbon (BC) concentrations were measured at 1-minute intervals using a multi-angle absorption photometer (MAAP; Thermo Fisher Scientific, Waltham, MA, USA). Total PM_1 mass was calculated as the sum of NR-PM_1 and BC.

Hourly trace gas concentrations (CO, O_3, NO_2, SO_2) were obtained from the Gireum air quality monitoring station (37.61° N, 127.03° E), managed by the Seoul Research Institute of Public Health and Environment. Meteorological data (temperature, RH, wind speed/direction) were collected from the nearby Jungreung site (37.61° N, 127.00° E). All data are reported in Korea Standard Time (UTC+9).

To examine aerosol volatility, a thermodenuder (TD; Envalytix LLC) was installed upstream of the HR-ToF-AMS. Details are provided in Supplementary Section S1 Kang et al. (2022). Briefly, ambient flow alternated every 5 minutes between a TD line and a bypass line at 1.1 L min^{-1}. Residence time in the TD line was ~6.3 s. The TD setup included a 50 cm heating section followed by an adsorption unit. Heated particles were stripped of volatile species, while the downstream carbon-packed section prevented recondensation. TD temperature cycled through 12 steps (30 to 200 °C), with each step lasting 10 min (total cycle = 120 min). AMS V and W modes were alternated during the same cycle. The heater was pre-adjusted to the next temperature while the bypass was active.

2.3 Data Analysis

2.3.1 Data analysis and OA Source Apportionment

HR-AMS data were processed using SQUIRREL v1.65B and PIKA v1.25B. Mass concentrations of non-refractory PM_1 (NR-PM_1) species were derived from V-mode data, while high-resolution mass spectra (HRMS) and the elemental composition of organic aerosols (OA) were obtained from W-mode data. 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 multiplicative, 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; $\Delta = 0.02 \approx 3.7\%$, 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. For organics, Eelemental ratios (O:C, H:C, and OM/OC) were calculated using the Improved-Ambient (IA) method (Canagaratna et al., 2015). Positive Matrix Factorization (PMF) was applied to the HRMS of organics using the PMF2 algorithm (v4.2, robust mode) (Paatero and Tapper, 1994). The HRMS and corresponding error matrices from PIKA were analyzed using the PMF Evaluation Tool v2.05 (Ulbrich et al., 2009). Data pretreatment followed established protocols (Ulbrich et al., 2009; Zhang et al., 2011).

A six-factor solution (fPeak = 0; Q/Q_expected = 3.56) was selected as optimal (Fig. S1). The resolved OA sources included 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), less-oxidized oxygenated OA (LO-OOA; 30%; O:C = 0.68), and more-oxidized oxygenated OA (MO-OOA; 20%; O:C = 1.15) (Figs. S2 and S3). Alternative five- and seven-factor solutions were also evaluated. In the five-factor solution, the biomass burning source was not clearly resolved and appeared to be distributed across multiple factors. In the seven-factor solution, BBOA was further split into two separate factors without clear distinction or added interpretive value, making the six-factor solution the most physically meaningful and interpretable (Figs. S4 and S5).

2.3.2 Thermogram and Volatility Estimation

The chemical composition dependent mass fraction remaining (MFR) was derived at each TD temperature by dividing the corrected mass concentration of the TD line [p] by the average of the adjacent bypass lines [p-1] and [p+1]. Thermograms were corrected for particle loss, estimated using reference substances like NaCl, which exhibit minimal evaporation (Huffman et al., 2009; Saha et al., 2014; Kang et al., 2023). OA factor concentrations at each TD temperature were derived via multivariate linear regression between post-TD HRMS and ambient OA factor HRMS profiles as described in Zhou et al., 2016.

Volatility distributions were modeled using the thermodenuder mass transfer model from Riipinen et al. (2010) and Karnezi et al. (2014), implemented in Igor Pro 9 (Kang et al., 2022). OA mass was distributed into eight logarithmic saturation concentration bins (C*: 1000 to 0.0001 $\mu g\ m^{-3}$). Modeled MFRs were fit to observations using Igor's "FuncFit" function, repeated 1,000 times per OA factor to determine best-fit results. The model assumes no thermal decomposition and includes adjustable parameters: mass accommodation coefficient (α_m) and enthalpy of vaporization (ΔH_{exp}), randomly sampled within literature-based ranges (Table S1).

3 Results and discussion

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3.1 Overview of PM_1 Composition and OA Sources

We conducted continuous measurements from 28 November to 28 December 2019, characterizing a winter period with a mean PM_1 concentration of 27.8±15.3 $\mu g m^{-3}$. 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 34.8 $\mu g m^{-3}$ (using a Korea-specific $PM_1/PM_{2.5} \approx 0.8$ (Kwon et al., 2023), which is near the national 24-h $PM_{2.5}$ standard (35 $\mu g m^{-3}$) (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.

~~The time series of submicron aerosol (PM_1 = NR-PM_1 + BC) mass concentrations measured by the AMS (non-refractory species) and MAAP (black carbon) are shown in Fig. S6, along with gaseous pollutants such as CO, SO_2, and O_x ($O_x = O_3 + NO_2$), and meteorological parameters including relative humidity (RH), temperature, wind direction, and wind speed. The mean PM_1 concentration during the study period was moderate, at 27.8 ± 15.3 $\mu g m^{-3}$.~~

Figure 1 summarizes the overall non-refractory submicron aerosol (NR-PM1) composition and the identified OA factors. Organics (41%) and nitrate (30%) were the most abundant chemical components of PM_1, followed by ammonium (12%), sulfate (10%), BC (5%), and chloride (3%) (Fig. 1a). 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 NOA, which will be discussed in detail in Section 3.1.1.

PM_1 mass concentrations varied widely, ranging from 4.61 to 91.4 μg m^{-3}, largely due to two severe haze episodes that occurred between December 7–12 and December 22–26 (Fig. 1). During these episodes, average concentrations increased significantly, driven primarily by elevated levels of nitrate, MO-OOA, and NOA (Fig. 1f,g). ~~These results suggest that the haze events were caused by local accumulation of emissions and enhanced SOA formation under stagnant meteorological conditions.~~ Back-trajectory clustering shows frequent short-range recirculation over the Seoul Metropolitan Area during haze (Cluster 1; Fig. S8), and the time series indicates

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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. Such haze episodes, characterized by local emission buildup and secondary aerosol production, are a typical wintertime feature, as also reported in Kim et al. (2017).

3.1.1 Nitrogen-containing organic aerosol (NOA)

Unlike previous wintertime aerosol studies in Seoul, this study successfully resolved a nitrogen-containing organic aerosol (NOA) factor by applying positive matrix factorization (PMF) to high-resolution AMS data. NOA contributed approximately 2% of the total organic aerosol (OA) mass—comparable to urban observations in Guangzhou (3%; Chen et al., 2021), Pasadena (5%; Hayes et al., 2013), and New York (5.8%; Sun et al., 2011).

Detection of particulate NOA using real time measurement has been challenging due to its low concentration and high volatility. Although Baek et al. (2022) identified nitrogen-containing species in Seoul via year-round filter-based molecular analysis, PMF-based resolution of NOA in real time has not been previously reported. The successful identification in this study is likely attributable to favorable winter meteorological conditions—specifically low temperatures (–0.24 °C) and persistently high relative humidity (~57%) compared to the 2017 winter season (Kim et al., 2017)—that enhanced gas-to-particle partitioning of semi-volatile amines, thereby enabling their detection (Fig. S2). NOA concentrations frequently exceeded 1 μg m^{-3} when RH surpassed 60% (Fig. 2), supporting the importance of RH-driven partitioning and the subsequent formation of low-volatility aminium salts (Rovelli et al., 2017). Although extremely low temperatures may inhibit NOA formation due to the transition of aerosol particles into solid phase (Ge et al., 2011; Srivastava et al., 2022), the combination of consistently cold and humid conditions during the measurement period likely promoted the partitioning of semi-volatile amines into the particle phase.

In addition, episodic haze events further elevated NOA levels, increasing its contribution to OA from 1% during clean periods to as much as 3% (Fig. 1f–h). These high-concentration events likely improved the signal-to-noise ratio, facilitating PMF resolution. 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; Hanson et al., 2014).

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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).

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.

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~~closely matching reference spectra of low-molecular-weight alkylamines such as dimethylamine (DMA), trimethylamine (TMA), methylamine (MA), and dibutylamine (DBA) (Fig. 3b-e). 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). While other amines like triethylamine (TEA), diethylamine (DEA), and ethylamine (EA) may contribute, their typical sources—such as industrial processes, solvent use, or wastewater treatment (E. Poste et al., 2014; He et al., 2016; Ge et al., 2011)—are distinct from biomass combustion, and thus they are considered less likely to be the dominant contributors under wintertime conditions in Seoul. Previous molecular analysis by Baek et al. (2022) also supports DMA, MA, and TMA as the main amine species observed during December in Seoul.~~

Supporting this, NOA exhibited a diurnal pattern similar to that of BBOA, with both peaking at night and in the early morning (Fig. 2a), suggesting shared sources or formation mechanisms. Biomass burning under cold, oxygen-limited conditions is known to emit various amines and amides (You et al., 2014; Yao et al., 2016), which may contribute directly to NOA or serve as precursors for its secondary formation. Strong correlations with CH_4N^+ (r = 0.95) and $C_2H_6N^+$ (r = 0.91) (Fig. 2) further support the presence of reduced nitrogen compounds, typically associated with residential fuel combustion and wintertime heating. However, the time series of NOA and BBOA were not well correlated (Fig. 2 and S7), likely because NOA episodes preferentially occurred during haze periods under stagnant conditions (Fig. 1), whereas BBOA emissions tend to follow a more regular, daily emission pattern. Under cold, humid, and stagnant conditions, these semi-volatile amines can readily partition into the particle phase and form low-volatility aminium salts, enhancing the observed NOA signal. Taken together, these results suggest that NOA during wintertime in Seoul is strongly influenced by a combination of combustion-related primary emissions and subsequent atmospheric processing of amine-containing species, facilitated by seasonally favorable conditions.

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3.1.2 Secondary organic aerosols (SOA)

In this study, two ~~oxygenated organic aerosol (~~OOA~~)~~ factors—more-oxidized OOA (MO-OOA) and less-oxidized OOA (LO-OOA)—were identified, together accounting for approximately half of the total organic aerosol (OA) mass. This fraction is notably higher than that reported in previous wintertime urban studies (Kim et al., 2017; Zhang et al., 2007). Both OOAs exhibited characteristic mass spectral features, including prominent peaks at *m/z* 44 (CO_2^+) and *m/z* 43 ($C_2H_3O^+$), which are widely recognized as markers of oxygenated organics (Fig. S2e, S3f). The oxygen-to-carbon (O:C) ratios for MO-OOA and LO-OOA were 1.15 and 0.68, respectively, indicating highly

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oxidized chemical compositions. The O:C ratio of MO-OOA was especially elevated, exceeding those reported in previous Seoul campaigns—0.68 in winter 2015 (Kim et al., 2017), 0.99 in spring 2019 (Kim et al., 2020), and 0.78 in fall 2019 (Jeon et al., 2023)—while the LO-OOA ratio was within a similar range.

MO-OOA showed strong correlations with secondary inorganic species such as nitrate (r = 0.90), ammonium (r = 0.92), and sulfate (r = 0.81), consistent with its formation through regional and local photochemical aging processes (Fig. S3). 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). ~~). In contrast, LO-OOA exhibited only moderate correlations with these inorganics (r = 0.50, 0.51, and 0.42, respectively), which may suggest an additional influence from other semi-primary sources not strongly associated with inorganic secondary species such as biomass burning.~~ 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. ~~This interpretation is further supported by a minor signal at m/z 60—indicative of levoglucosan, a known tracer for biomass burning (Fig. S2). The weaker coupling with secondary inorganics implies that LO-OOA may represent a mixture of aged and semi-primary organics, partially derived from combustion-related activities~~.

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3.1.3 Primary organic aerosols (POA)

Three primary organic aerosol (POA) factors were identified in this study: hydrocarbon-like OA (HOA), cooking-related OA (COA), and biomass burning OA (BBOA). These three components exhibited mass spectral and temporal characteristics consistent with previous observations in Seoul and other urban environments. HOA was characterized by dominant alkyl fragment ions ($C_nH_{2n+1}^+$ and $C_nH_{2n-1}^+$; Fig. S2a) and a low O:C ratio (0.13), consistent with traffic-related emissions (0.05–0.25) (Canagaratna et al., 2015). It showed strong correlations with vehicle-related ions $C_3H_7^+$ (r = 0.79) and $C_4H_9^+$ (r = 0.86) (Kim et al., 2017; Canagaratna et al., 2004; Zhang et al.,

2005), and exhibited a distinct morning rush hour peak (06:00–08:00), followed by a decrease likely driven by boundary layer expansion (Fig. S3a).

COA, accounting for 21% of OA, showed higher contributions from oxygenated ions than HOA, with tracer peaks at *m/z* 55,84 and 98 (Fig. S2b) consistent with cooking emissions (Sun et al., 2011). It correlated strongly with cooking-related ions such as $C_3H_3O^+$ (r = 0.94), $C_5H_8O^+$ (r = 0.96), and $C_6H_{10}O^+$ (r = 0.98) (Fig. S3h), and displayed prominent peaks during lunch and dinner hours, reflecting typical cooking activity patterns.

BBOA was identified based on characteristic ions at *m/z* 60 ($C_2H_4O_2^+$) and 73 ($C_3H_5O^+$), both of which are associated with levoglucosan—a well-established tracer for biomass burning (Simoneit et al., 2002). Its relatively high f_{60} and low f_{44} values (Fig. S8a) indicate that the BBOA observed in this study was relatively fresh and had not undergone extensive atmospheric aging (Cubison et al., 2011). Furthermore, BBOA exhibited moderate correlations with NOA in both diurnal profiles and time series (Fig. 2), particularly with nitrogen-containing ions such as $C_2H_4N^+$ (r = 0.67) and $C_2H_6N^+$ (r = 0.56) (Fig. 2 and S3), which are also dominant peaks in the NOA mass spectrum. This overlap suggests a potential shared emission source or co-emission scenario, ~~such as biomass burning~~, ~~which is known~~consistent with the co-emission of ~~to emit~~ both organic aerosols and reduced nitrogen-containing compounds. 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.

3.2 Volatility of Non-Refractory Species

Figure 4 presents thermograms of non-refractory (NR) species measured by HR-ToF-AMS. The mass fraction remaining (MFR) after thermodenuder (TD) treatment follows the typical volatility trend reported in previous studies (Xu et al., 2016; Kang et al., 2022; Jeon et al., 2023; Huffman et al., 2009): nitrate was the most volatile, followed by chloride, ammonium, organics, and sulfate. Nitrate showed the steepest decline with temperature, with

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a T_{50} of ~67 °C—higher than pure ammonium nitrate (~37 °C; Huffman et al., 2009), suggesting contributions from less volatile species like organonitrates or metal nitrates (Feng et al., 2023). Nearly complete evaporation occurred by 200 °C (~2% remaining). 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). ~~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.~~ Sulfate was the least volatile (T_{50} ≈ 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~~Sulfate was the least volatile (T_{50} ~ 170 °C), consistent with ammonium sulfate (Scott and Cattell, 1979). A subtle slope change near 140 °C may suggest phase transitions or less volatile sulfate components.~~ About 25% remained at 200 °C, indicating possible contributions from metallic or organic sulfates. Ammonium showed intermediate volatility, with T_{50} between nitrate and sulfate. Its slightly lower winter T_{50} suggests stronger nitrate association. Residual ammonium at 200 °C was consistent (~4%) in previously reported spring/fall measurements (Kang et al., 2022; Jeon et al., 2023).~~Residual ammonium at 200 °C was consistent (~ 4%) across seasons (Kang et al., 2022; Jeon et al., 2023)~~. 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.~~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~~.

~~Organic aerosol (~~OA~~)~~ exhibited moderate volatility (T_{50} ~120 °C), consistent with the presence of a wide variety of compounds with differing volatilities. This trend aligns with previously reported spring and fall observations in Seoul, Korea (Kang et al., 2022; Jeon et al., 2023).~~This trend aligns with spring and fall observations (Kang et al., 2022; Jeon et al., 2023).~~

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3.2.1 Volatility Profiles of Organic sources

Figure 5 presents the volatility distributions of six OA sources within the volatility basis set (VBS) framework. Volatility is expressed as the effective saturation concentration (C*, μg m^{-3}), where higher C* values correspond to higher volatility. Following Donahue et al. (2009), C* values are categorized into four bins: extremely low-volatility organic compounds (ELVOCs, log C* < –4.5), low-volatility organic compounds (LVOCs, –4.5 < log

C* < –0.5), semi-volatile organic compounds (SVOCs, –0.5 < log C* < 2.5), and intermediate-volatility organic compounds (IVOCs, 2.5 < log C* < 6.5).

Among the primary OA (POA) sources, hydrocarbon-like OA (HOA) exhibited the highest volatility, with mass predominantly distributed in the SVOC and IVOC ranges. This is consistent with its low oxidation state (O:C = 0.35) and primary emission characteristics. 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), and had lower O:C ratios of 0.25 and 0.19, respectively. Their slightly more oxidized nature relative to HOA, despite a similar volatility range, may reflect emissions occurring under nighttime or cooler conditions, which promote condensation of otherwise volatile species. The similar volatility distributions and MFR profiles of BBOA and NOA (Fig. S9) further support the possibility of a shared emission source or formation pathway (Section 3.1.1). Cooking-related OA (COA) showed a more moderate volatility profile, with mass more evenly distributed across the LVOC and SVOC bins. This pattern reflects its diverse cooking sources and variable emission profiles as previously reported (Kang et al., 2022).~~This pattern reflects its diverse cooking sources and variable emission profiles (Kang et al., 2022)~~.

For secondary OA (SOA), less-oxidized oxygenated OA (LO-OOA) exhibited the lowest volatility, with substantial mass in the LVOC and ELVOC bins (C* ≈ 10^{-3}–10^{-4})~~, consistent with its aged, highly condensed nature~~. This is in agreement with previous findings in Seoul during spring (Kang et al., 2022). In contrast, more-oxidized OOA (MO-OOA), despite its higher oxidation state (O:C = 1.15), displayed greater volatility, with a peak at C* ≈ 10^{1}. This discrepancy likely reflects differences in formation and aging processes, as discussed further in Section 3.~~2.5~~3.

Overall, the volatility characteristics across OA factors suggest that oxidation state alone does not fully explain volatility. Rather, volatility is shaped by a combination of emission source, emission timing, temperature, and atmospheric processing. These findings highlight the importance of integrating both chemical and physical characterization to better understand OA formation and aging across seasons.

3.3 Aging effect on volatility from 2D VBS

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~~n~~ 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).

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.

3.3.1 Proposed Mechanism: Fragmentation and Condensation under Low-OH Haze

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~~This observation appears to contradict the expected inverse relationship between O:C and volatility but may be explained by alternative oxidation mechanisms and specific environmental conditions.~~

MO-OOA concentrations increased during haze episodes—characterized by reduced ozone levels, low solar radiation and elevated aerosol mass concentrations (Fig. 6 and Fig. S6, yellow shading). The suppressed ozone likely indicates lower OH radical production via O_3 photolysis, leading to a low-OH oxidation regime. 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).Under such conditions, particle-phase autoxidation involving RO_2 radicals can become the dominant oxidation pathway. 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. These processes tend to produce highly oxidized but relatively low–molecular-weight products (Ehn et al., 2014; Zhao et al., 2023). Unlike classical OH-initiated, multi-generational aging—which increases molecular mass and reduces volatility—fragmentation-dominated oxidation can cleave larger precursors into smaller oxygenated compounds, resulting in higher volatility despite elevated O:C. 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). Furthermore, high aerosol mass loadings during haze events provide abundant surface area for the uptake of semi-volatile/intermediate-volatility organics 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). ~~species~~. This facilitates the condensation of even relatively volatile, oxidized compounds onto particles (Fig. 6). The net result is an apparent increase in both oxidation state and volatility of OA, as reported in aging studies under stagnant and polluted conditions (Jimenez et al., 2009; Ng et al., 2016).

In line with these reports, our results also revealed a decoupling between O:C and volatility, with MO-OOA showing high volatility despite its elevated O:C ratio (~1.15). While this behavior has been observed in other urban

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environments, this study provides one of the first detailed thermodynamic assessments of this decoupling under winter haze conditions in Seoul using real-time TD-AMS measurements. Supporting this interpretation, MO-OOA in this study was characterized by a consistently high f_{44} (CO_2^+) signal and a relatively stable f_{43} ($C_2H_3O^+$) signal compared to LO-OOA (Fig. S8b). During specific periods when MO-OOA concentrations increased, only f_{44} was noticeably enhanced, while f_{43} remained flat (Fig. 6). This temporal pattern—elevated f_{44} without corresponding changes in f_{43}—is a typical signature of highly oxidized and fragmented organic aerosol and suggests advanced aging dominated by fragmentation rather than functionalization (Kroll et al., 2009). 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.

~~Thus, although MO-OOA had a high O:C ratio, its elevated volatility likely reflects oxidation dominated by autoxidation, fragmentation, and condensation of small oxygenated fragments under conditions of limited OH availability and high particulate surface area.~~

This unexpected volatility behavior of highly oxidized MO-OOA highlights the need for secondary organic aerosol (SOA) models to incorporate fragmentation-dominated oxidation pathways—especially under haze conditions where conventional assumptions linking O:C to volatility may break down. Including such mechanisms could improve model accuracy in representing OA aging and volatility in urban air quality simulations.

4 Conclusions

This study offers a detailed characterization of wintertime submicron aerosols (PM_1) in Seoul by integrating chemical composition, volatility behavior, and source apportionment to better understand their formation and atmospheric evolution. Organic aerosols (OA), particularly secondary organic aerosols (SOA), were the dominant PM_1 component, highlighting the significance of oxidative processes even during cold seasons. A notable result is the successful real-time resolution of a nitrogen-containing organic aerosol (NOA) factor, enabled by cold, humid meteorological conditions that enhanced the partitioning and stabilization of amine-derived compounds. The NOA factor was characterized by tracer ions associated with low-molecular-weight alkylamines such as TMA, DMA, and MA, which likely originated from biomass combustion.

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Volatility analysis revealed distinct thermodynamic behavior across OA sources. Primary OA factors such as HOA, BBOA, and COA exhibited relatively high volatility, while LO-OOA showed low volatility and a higher oxidation state, consistent with aged, low-volatility material. The similarity in volatility distributions and diurnal patterns between BBOA and NOA suggests that biomass combustion under wintertime conditions is a likely contributor to both primary organic and nitrogenous aerosol formation.

Interestingly, MO-OOA—despite its high oxygen-to-carbon (O:C) ratio—exhibited elevated volatility, diverging from the expected inverse relationship between oxidation state and volatility. This suggests that under stagnant, polluted conditions with suppressed ozone and OH radical levels, particle-phase autoxidation and fragmentation pathways may dominate over traditional OH-initiated aging, yielding highly oxidized yet semi-volatile products. These findings highlight the importance of coupling high-resolution chemical and physical aerosol measurements to better understand OA formation processes and properties within urban air quality frameworks. Consequently, air quality models should incorporate diverse oxidation mechanisms and avoid assuming a direct link between oxidation state and volatility.

Acknowledgements

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Author Contributions

Hwajin Kim designed and prepared the manuscript. Jiwoo Jeong operated the TD-AMS and analyse the data. Jihye Moon analyse the data. Hyungu Kang analyse the volatility of OA.

Conflicts of Interest

Authors declare that they have no conflict of interest.

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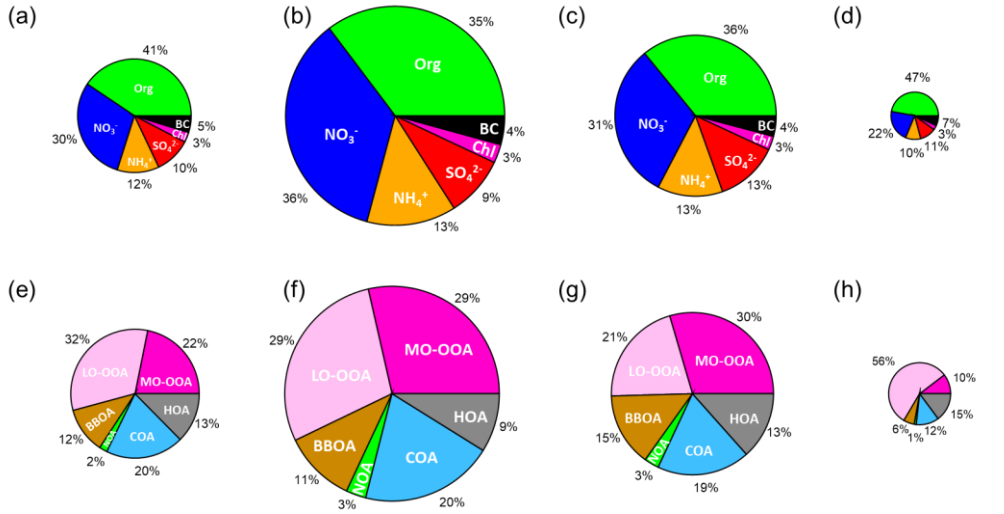
Tables and Figures



	Period	Standard	Avg. Mass conc.(μg m^{-3})
Total	2019.11.28 ~ 2019.12.28		Avg PM_1 = 26.37
Clean	2019.12.04 ~ 2019.12.06	Daily PM_1 < 10.00 μg m^{-3}	Avg PM_1 = 9.98
Haze 1	2019.12.07 ~ 2019.12.11	Daily PM_1 > 30.00 μg m^{-3}	Avg PM_1 = 51.88
Haze 2	2019.12.21 ~ 2019.12.25	Daily PM_1 > 30.00 μg m^{-3}	Avg PM_1 = 37.71

Figure 1. Compositional pie charts of PM_1 species for (a) the entire study period, (b) haze period 1, (c) haze period 2, and (d) a clean period; and of each OA source for (e) the entire study period, (f) haze period 1, (g) haze period 2, and (h) the clean period.Table. Standard and average PM_1 mass concentrations during the entire study period, haze period 1, haze period 2, and the clean period.

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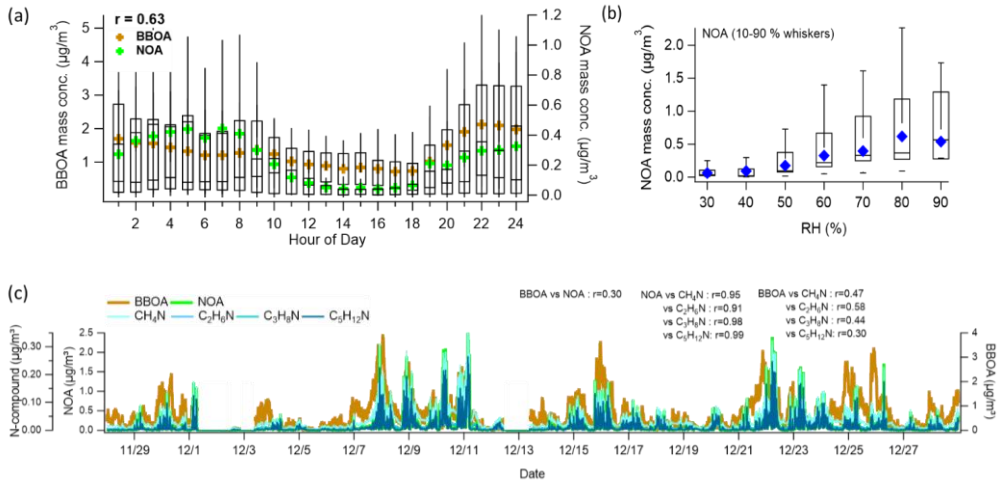

Figure 2. (a) Diurnal mean profiles of NOA and BBOA. Whiskers denote the 90th and 10th percentiles; box edges represent the 75th and 25th percentiles; the horizontal line indicates the median, and the colored marker shows the mean. The diurnal correlation between NOA and BBOA mean values is 0.63. (b) Relative humidity (RH)-binned nighttime (19:00–05:00) profile of NOA. Box and whisker definitions are the same as in panel (a). (c) Time series of NOA, BBOA, and amine-related ions (CH_4N^+, $C_2H_6N^+$, $C_3H_8N^+$, $C_5H_{12}N^+$), along with their correlations with NOA and BBOA.

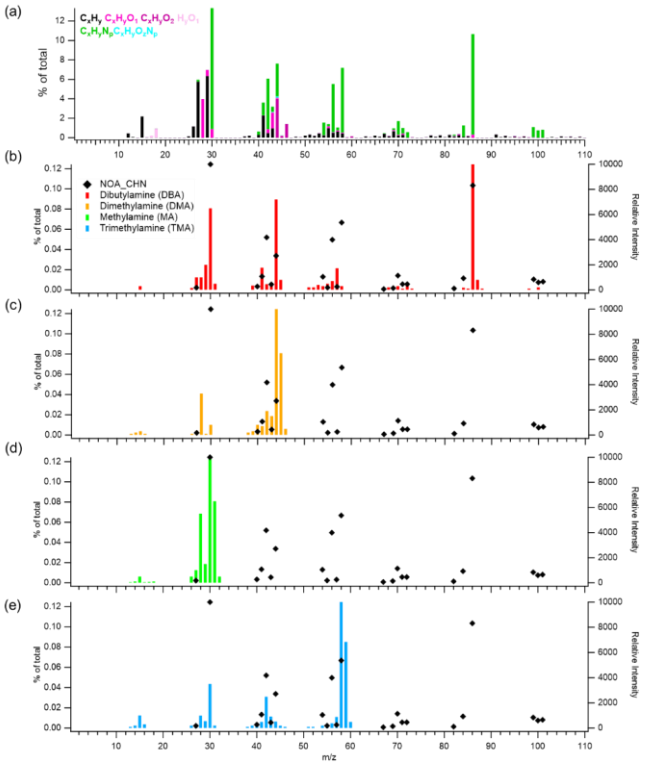

Figure 3. Mass spectra of (a) the NOA factor resolved by PMF analysis in this study, and reference spectra of amines from the NIST library: (b) dibutylamine (DBA), (c) dimethylamine (DMA), (d) methylamine (MA), and (e) trimethylamine (TMA). In panels (b)–(e), the left y-axis indicates the contribution of CHN-containing ions in the NOA factor (% of total), while the right y-axis shows the relative intensity of each compound's mass spectrum from the NIST library.

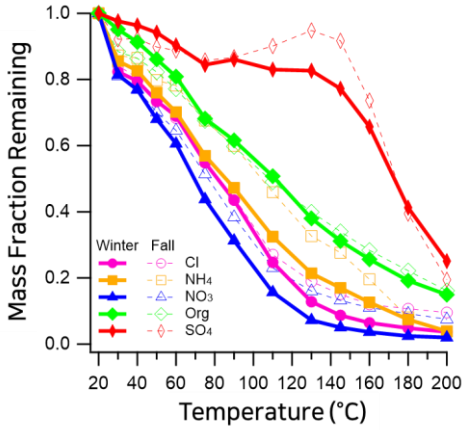

Figure 4. Mass fraction remaining (MFR) of non-refractory (NR) aerosol species measured in Seoul ~~during fall (solid lines) and winter (dashed lines) 2019~~ using a thermodenuder coupled to a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS). Winter 2019 (this study; dashed) is compared with fall 2019 (previously reported; solid) (Jeon et al., 2023).Species include organics (magenta), nitrate (blue), sulfate (orange), ammonium (green), and chloride (red).

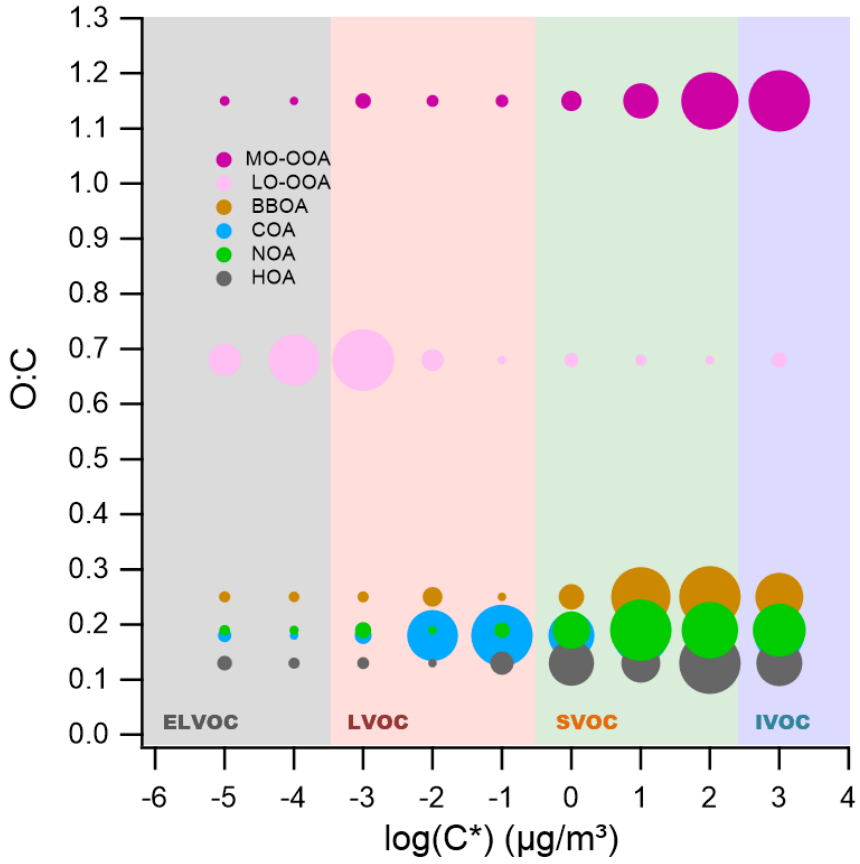

Figure 5. Two-dimensional volatility basis set (2D-VBS) representation of organic aerosol (OA) sources identified in winter 2019 in Seoul. The plot illustrates the relationship between the oxygen-to-carbon (O:C) ratio and the effective saturation concentration (C*) for each OA source resolved via positive matrix factorization (PMF). Solid circles represent the volatility distribution across C* bins, with marker size proportional to the mass fraction within each bin for the given source. Shaded regions correspond to different volatility classes: extremely low-volatility organic compounds (ELVOCs), low-volatility organic compounds (LVOCs), semi-volatile organic compounds (SVOCs), and intermediate-volatility organic compounds (IVOCs), delineated by their C* values.

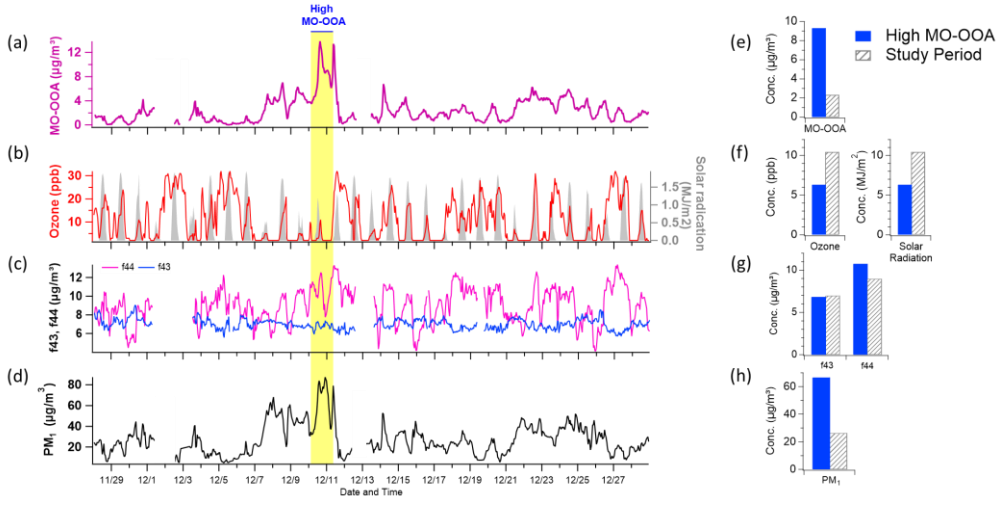

Figure 6. Time series plots of (a) MO-OOA concentration, (b) ozone (O_3) and solar radiation, (c) f_{44} and f_{43} (indicative of oxidation state), and (d) total PM_1 concentration. The period characterized by elevated MO-OOA levels is highlighted in bright yellow. Panels (e)–(f) present comparative distributions of these variables—MO-OOA, O_3 and solar radiation, f_{44} and f_{43}, and PM_1—between the high MO-OOA period (shaded in blue) and the entire measurement period (indicated by gray hatching).

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