https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

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

Hwajin Kim[1,2,*] Jiwoo Jeong[1], Jihye Moon[1], Hyun Gu Kang[2,3]

[1]Department of Environmental Health Sciences, Graduate School of Public Health, Seoul National University, 08826 Seoul, South Korea
[2]Institute of Health and Environment, Graduate School of Public Health, Seoul National University, 08826 Seoul, South Korea
[3]Now at Multiphase Chemistry Department, Max Planck Institute for Chemistry, 55128 Mainz, Germany

Correspondence to: Hwajin Kim (khj0116@snu.ac.kr)

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

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

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). 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). 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

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

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. 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) 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

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

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

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). Data were acquired at 2.5-minute intervals, alternating between V and W modes. The V mode 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

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

elemental composition of organic aerosols (OA) were obtained from W-mode data. Elemental 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 μg 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

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

3.1 Overview of PM_1 Composition and OA Sources

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 μg m^{-3}.

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. 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

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

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 (Milic et al., 2016). 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.

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. Its mass spectrum was dominated by amine-related fragments including m/z 30 (CH_4N^+), 44 ($C_2H_6N^+$), 58, and 86 (Fig. 3a), 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

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

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.

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 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 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. 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

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

secondary inorganics implies that LO-OOA may represent a mixture of aged and semi-primary organics, partially derived from combustion-related activities.

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 to emit both organic aerosols and reduced nitrogen-containing compounds.

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,

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

followed by chloride, ammonium, organics, and sulfate. Nitrate showed the steepest decline with temperature, with 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 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 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%) across seasons (Kang et al., 2022; Jeon et al., 2023). 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 spring and fall observations (Kang et al., 2022; Jeon et al., 2023).

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*, $\mu g\, m^{-3}$), 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

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

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 (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 ($C^* \approx 10^{-3}$–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 $C^* \approx 10^{1}$. This discrepancy likely reflects differences in formation and aging processes, as discussed further in Section 3.2.5.

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, the effective saturation concentration (C*) typically decreases, resulting in lower volatility (Donahue et al., 2006; Jimenez et al., 2009). This relationship arises because 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. Moreover, oxidative aging often leads to oligomerization or functionalization, promoting particle-phase retention.

However, in this study, the most oxidized OA factor—MO-OOA, with an 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

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

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. Under such conditions, particle-phase autoxidation involving RO_2 radicals can become the dominant oxidation pathway. 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. Furthermore, high aerosol mass loadings during haze events provide abundant surface area for the uptake of semi-volatile 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 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).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

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

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.

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.

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (RS-2025-00514570), the project "development of SMaRT based aerosol measurement and analysis systems for the evaluation of climate change and health risk assessment" operated by Seoul National University (900-20240101).

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.

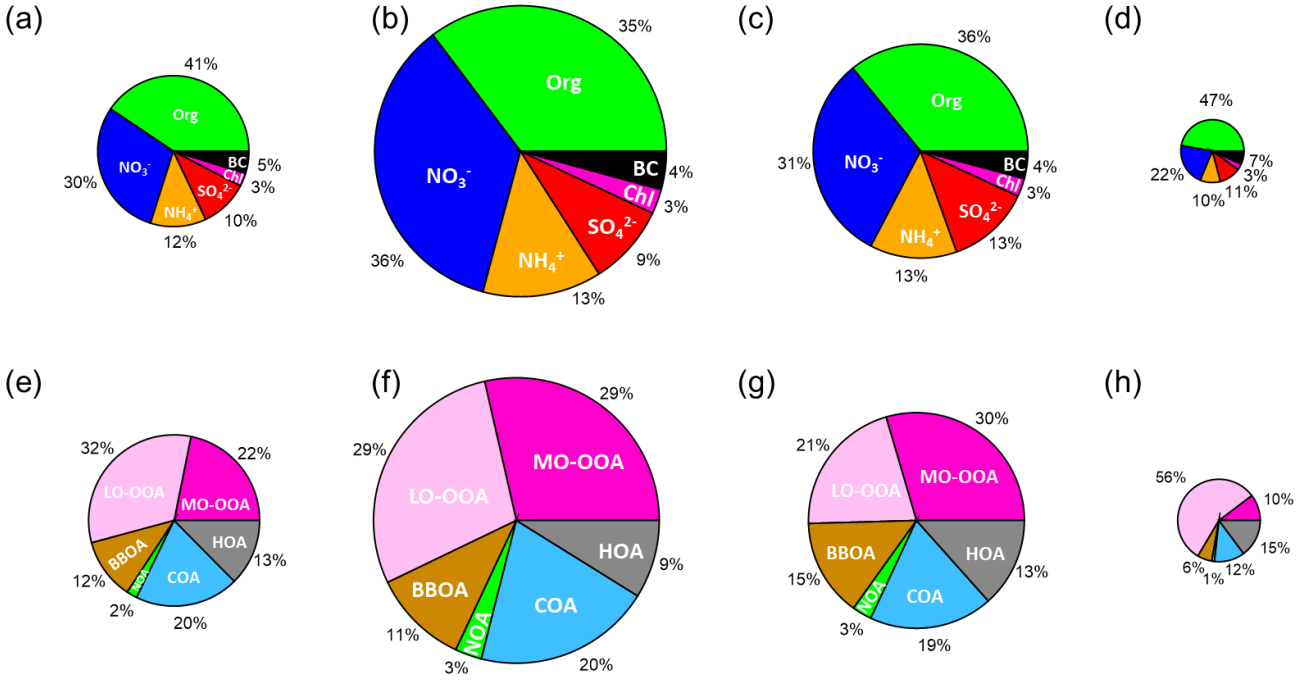
https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

391 **Tables and Figures**

392

393

394



395

	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

396

397 **Figure 1.** Compositional pie charts of PM_1 species for (a) the entire study period, (b) haze period 1, (c) haze period 2, and
398 (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
399 clean period.Table. Standard and average PM_1 mass concentrations during the entire study period, haze period 1, haze period
400 2, and the clean period.

401

402

403

404

405

406

407

408

409

410

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

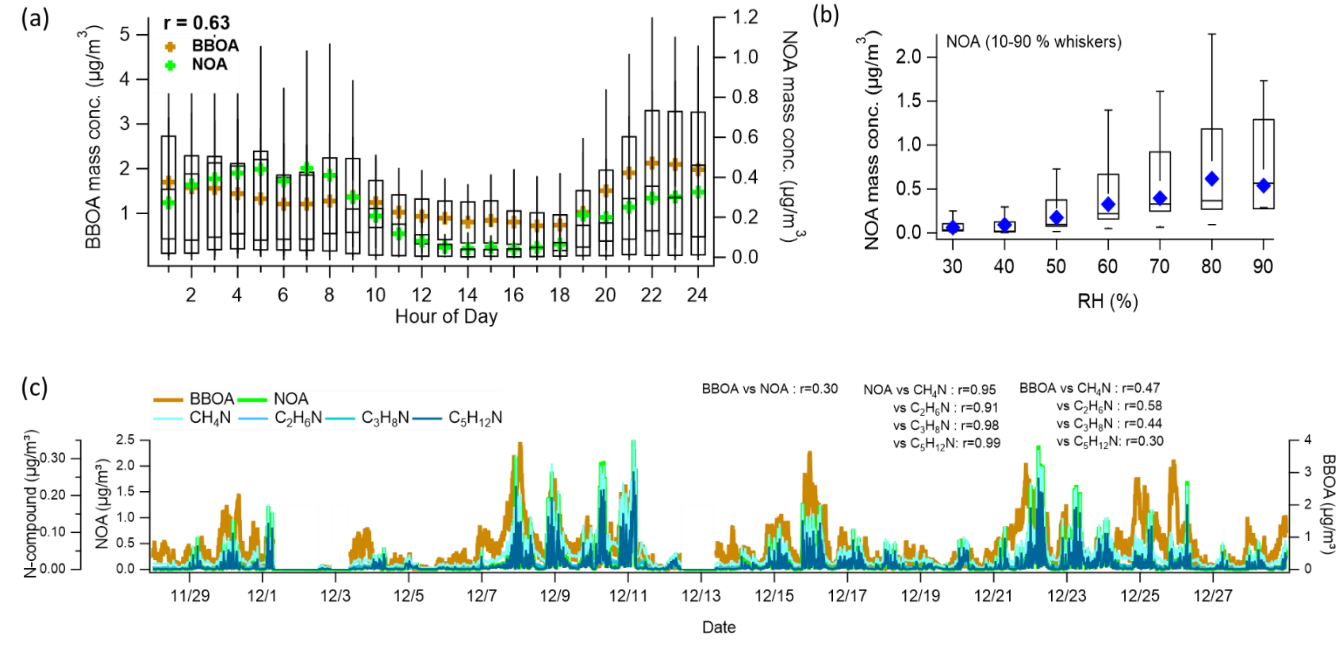


Figure 2. (a) Diurnal mean profiles of NOA and BBOA. Whiskers denote the 90th and 10th percentiles; box edges represent the 75th and 25th percentiles; the horizontal line indicates the median, and the colored marker shows the mean. The diurnal correlation between NOA and BBOA mean values is 0.63. (b) 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.

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

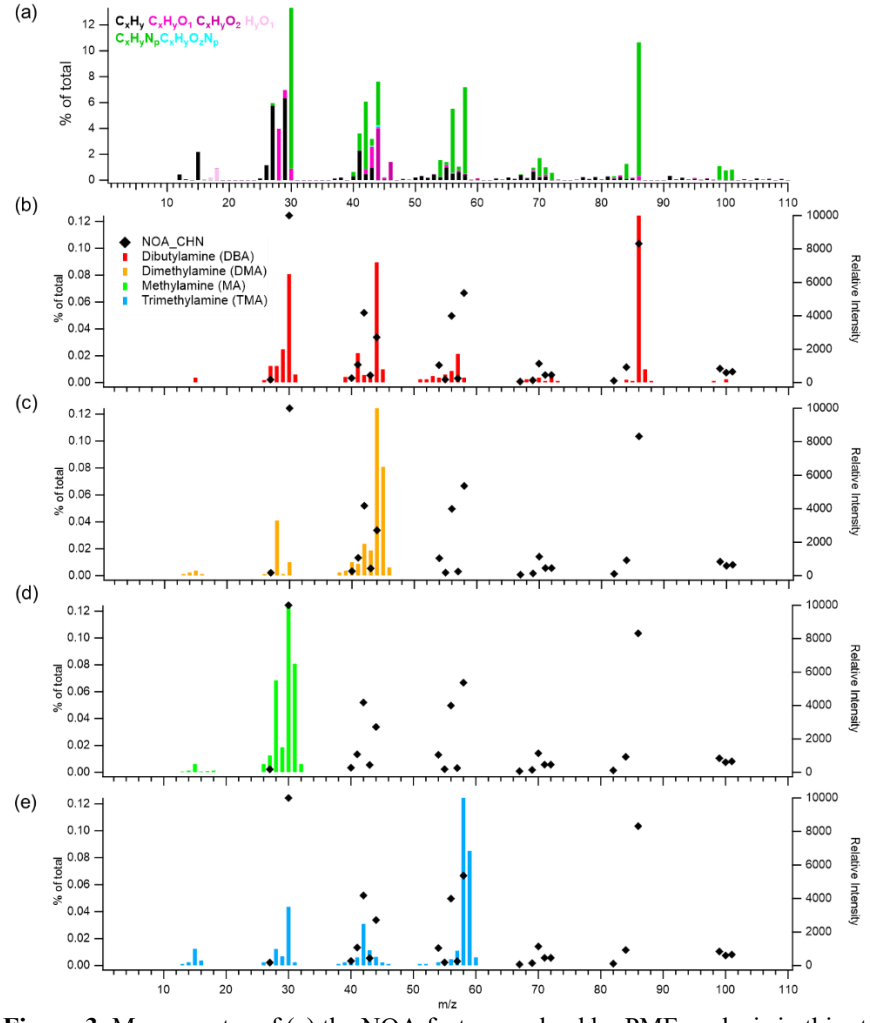
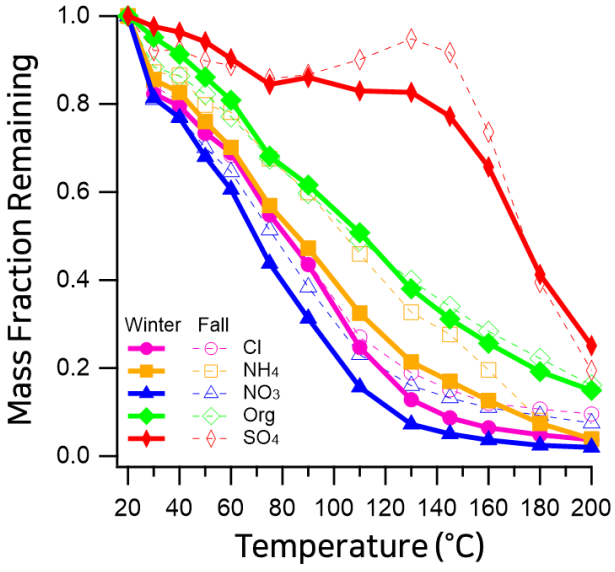


Figure 3. Mass spectra of (a) the NOA factor resolved by PMF analysis in this study, and reference spectra of amines from the NIST library: (b) dibutylamine (DBA), (c) dimethylamine (DMA), (d) methylamine (MA), and (e) trimethylamine (TMA). In panels (b)–(e), the left y-axis indicates the contribution 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.

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025



429 **Figure 4.** Mass fraction remaining (MFR) of non-refractory (NR) aerosol species measured in Seoul during fall (solid lines)
430 and winter (dashed lines) 2019 using a thermodenuder coupled to a high-resolution time-of-flight aerosol mass spectrometer
431 (HR-ToF-AMS). Species include organics (magenta), nitrate (blue), sulfate (orange), ammonium (green), and chloride (red).

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

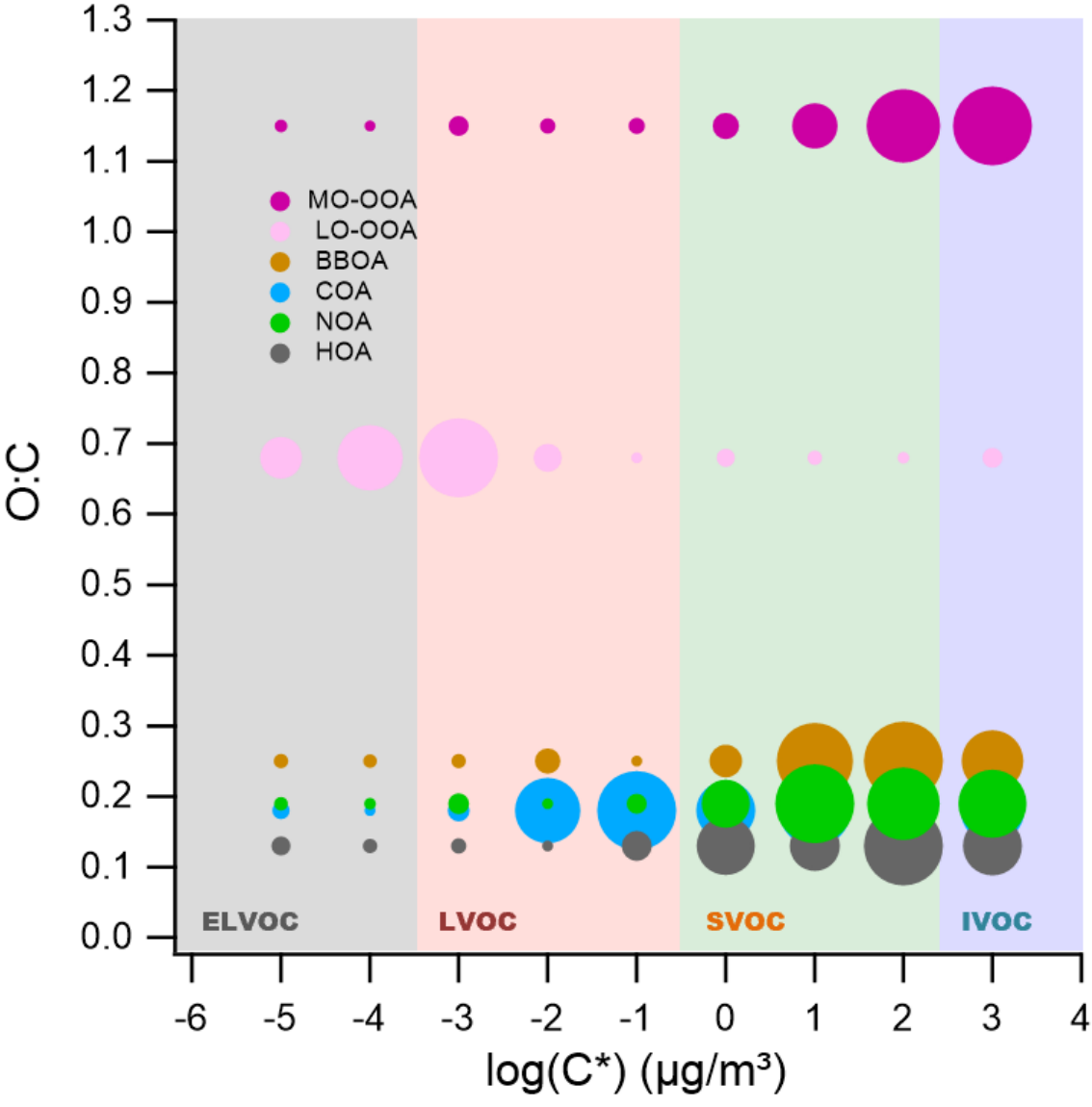


Figure 5. Two-dimensional volatility basis set (2D-VBS) representation of organic aerosol (OA) sources identified in winter 2019 in Seoul. The plot illustrates the relationship between the oxygen-to-carbon (O:C) ratio and the effective saturation concentration (C*) for each OA source resolved via positive 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.

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

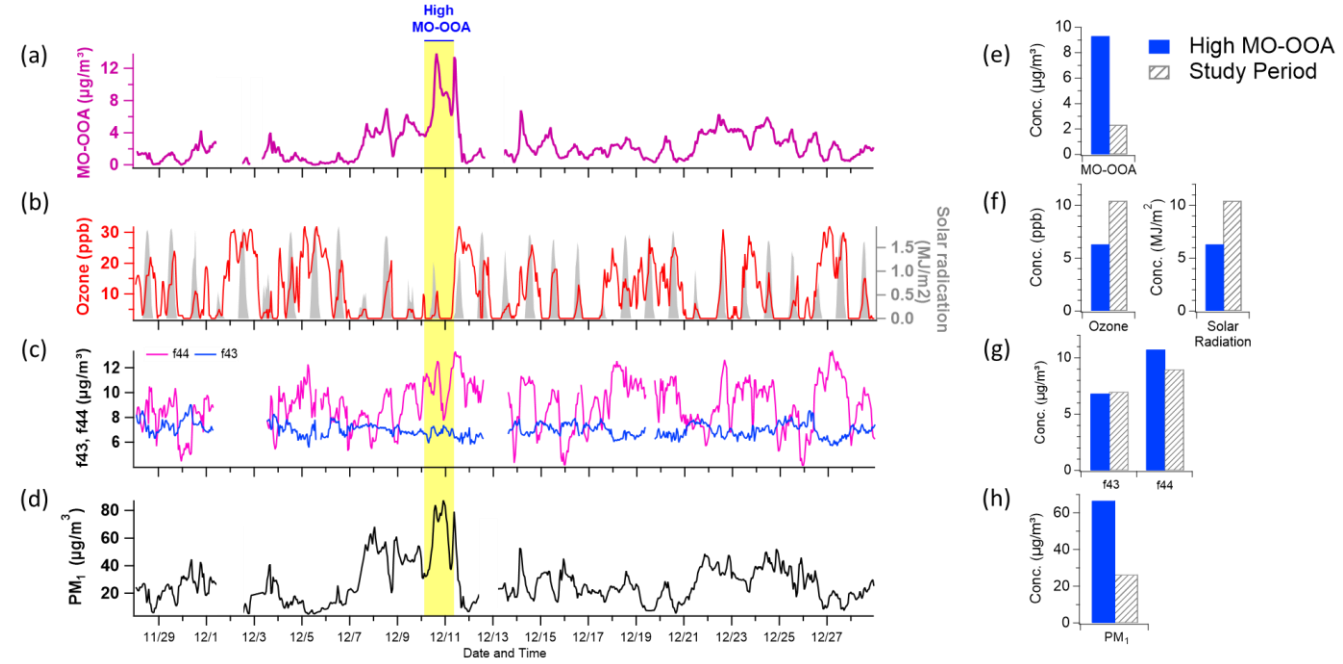


Figure 6. Time series plots of (a) MO-OOA concentration, (b) ozone (O_3) and solar radiation, (c) f_{44} and f_{43} (indicative of oxidation state), and (d) total PM_1 concentration. The period characterized by elevated MO-OOA levels is highlighted in bright yellow. Panels (e)–(f) present comparative 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).

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

References

Ghim, Y. S., Moon, K.-C., Lee, S., Kim, Y. P., 2005. Visibility trends in Korea during the past two decades. J. Air Waste Manag. Assoc. 55, 73–82. https://doi.org/10.1080/10473289.2005.10464599

Zhao, H., Che, H., Zhang, X., Ma, Y., Wang, Y., Wang, H., Wang, Y., 2013. Characteristics of visibility and particulate matter (PM) in an urban area of Northeast China. Atmos. Pollut. Res. 4, 427–434. https://doi.org/10.5094/APR.2013.049

Hamanaka, R. B., Mutlu, G. M., 2018. Particulate matter air pollution: Effects on the cardiovascular system. Front. Endocrinol. 9, 680. https://doi.org/10.3389/fendo.2018.00680

Manisalidis, I., Stavropoulou, E., Starvropoulos, A., Bezirtzoglou, E., 2020. Environmental and health impacts of air pollution: a review. Front. Public Health 8, 14. https://doi.org/10.3389/fpubh.2020.00014

IPCC, 2021. Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change, edited by Masson-Delmotte, V., Zhai, P., Pirani, A., Connors, S.L., Péan, C., Berger, S., et al. Cambridge University Press, Cambridge, UK and New York, NY, USA, pp. 817–922. https://doi.org/10.1017/9781009157896.008

Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M. R., Takami, A., Middlebrook, A. M., Sun, Y. L., Dzepina, K., Dunlea, E., Docherty, K., DeCarlo, P., Salcedo, D., Onasch, T. B., Jayne, J. T., Miyoshi, T., Shimono, A., Hatakeyama, N., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Weimer, S., Demerjian, K. L., Williams, P. I., Bower, K. N., Bahreini, R., Cottrell, L., Griffin, R. J., Rautianen, J., Worsnop, D. R., 2007. Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere mid-latitudes. Geophys. Res. Lett. 34, L13801. https://doi.org/10.1029/2007GL029979

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., ... Worsnop, D. R., 2009. Evolution of organic aerosols in the atmosphere. Science 326, 1525–1529. https://doi.org/10.1126/science.1180353

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., ... Seinfeld, J. H., 2009. The formation, properties and impact of secondary organic aerosol: current and emerging issues. Atmos. Chem. Phys. 9, 5155–5236. https://doi.org/10.5194/acp-9-5155-2009

Robinson, A. L., Donahue, N. M., Shrivastava, M. K., Weitkamp, E. A., Sage, A. M., Grieshop, A. P., Lane, T. E., Pierce, J. R., Pandis, S. N., 2007. Rethinking organic aerosols: Semivolatile emissions and photochemical aging. Science 315, 1259–1262. https://doi.org/10.1126/science.1133061

Donahue, N. M., Robinson, A. L., Stanier, C. O., Pandis, S. N., 2006. Coupled partitioning, dilution, and chemical aging of semivolatile organics. Environ. Sci. Technol. 40, 2635–2643. https://doi.org/10.1021/es052297c

Ng, N. L., Canagaratna, M. R., Zhang, Q., Jimenez, J. L., Tian, J., Ulbrich, I. M., Kroll, J. H., Docherty, K. S., Chhabra, P. S., Bahreini, R., Murphy, S. M., Seinfeld, J. H., Hildebrandt, L., Donahue, N. M., DeCarlo, P. F., Lanz, V. A., Prévôt, A. S. H., Dinar, E., Rudich, Y., Worsnop, D. R., 2010. Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry. Atmos. Chem. Phys. 10, 4625–4641. https://doi.org/10.5194/acp-10-4625-2010

Cappa, C. D., Jimenez, J. L., 2010. Quantitative estimates of the volatility of ambient organic aerosol. Atmos. Chem. Phys. 10, 5409–5424. https://doi.org/10.5194/acp-10-5409-2010

Sinha, A., George, I., Holder, A., Preston, W., Hays, M., Grieshop, A. P., 2023. Development of volatility distributions for organic matter in biomass burning emissions. Environ. Sci. Adv. 3, 11–23. https://doi.org/10.1039/D2EA00080F

Glasius, M., Goldstein, A. H., 2016. Recent discoveries and future challenges in atmospheric organic chemistry. Environ. Sci. Technol. 50, 2754–2764. https://doi.org/10.1021/acs.est.5b05105

Matsui, H., Koike, M., Takegawa, N., Kondo, Y., Griffin, R. J., Miyazaki, Y., Yokouchi, Y., Ohara, T., 2009. Secondary organic aerosol formation in urban air: Temporal variations and possible contributions from unidentified hydrocarbons. J. Geophys. Res. Atmos. 114, D02209. https://doi.org/10.1029/2008JD010164

Jiang, F., Liu, Q., Huang, X., Wang, T., Zhuang, B., Xie, M., 2012. Regional modelling of secondary organic aerosol over China using WRF/Chem. J. Aerosol Sci. 53, 50–61. https://doi.org/10.1016/j.jaerosci.2011.09.003

Li, J., Zhang, M., Wu, F., Sun, Y., Tang, G., 2017. Assessment of the impacts of aromatic VOC emissions and yields of SOA on SOA concentrations with the air quality model RAMS-CMAQ. Atmos. Environ. 158, 105–115. https://doi.org/10.1016/j.atmosenv.2017.03.035

Zhao, B., Wang, S., Donahue, N. M., Jathar, S. H., Huang, X., Wu, W., ... & Hao, J. (2016). Quantifying the effect of organic aerosol aging and intermediate-volatility emissions on regional-scale aerosol pollution in China. Scientific Reports, 6, 28815. https://doi.org/10.1038/srep28815

Kang, H. G., Kim, Y., Collier, S., Zhang, Q., Kim, H., 2022. Volatility of springtime ambient organic aerosol derived with thermodenuder aerosol mass spectrometry in Seoul, Korea. Environ. Pollut. 310, 119203. https://doi.org/10.1016/j.envpol.2022.119203

Huang, X.-F., He, L.-Y., Hu, M., Canagaratna, M. R., Sun, Y., Zhang, Q., Worsnop, D. R., 2010. Highly time-resolved chemical characterization of atmospheric submicron particles during 2008 Beijing Olympic Games using an Aerodyne

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

High-Resolution Aerosol Mass Spectrometer. Atmos. Chem. Phys. 10, 8933–8945. https://doi.org/10.5194/acp-10-8933-2010

Mohr, C., DeCarlo, P. F., Heringa, M. F., Chirico, R., Slowik, J. G., Richter, R., Reche, C., Alastuey, A., Querol, X., Seco, R., Peñuelas, J., Jiménez, J. L., Crippa, M., Zimmermann, R., Baltensperger, U., Prévôt, A. S. H., 2012. Identification and quantification of organic aerosol from cooking and other sources in Barcelona using aerosol mass spectrometer data. Atmos. Chem. Phys. 12, 1649–1665. https://doi.org/10.5194/acp-12-1649-2012

Xu, L., Kollman, M. S., Song, C., Shilling, J. E., Ng, N. L., 2014. Effects of NOx on the volatility of secondary organic aerosol from isoprene photooxidation. Environ. Sci. Technol. 48, 2253–2262. https://doi.org/10.1021/es404842g

Grieshop, A. P., Logue, J. M., Donahue, N. M., Robinson, A. L., 2009. Laboratory investigation of photochemical oxidation of organic aerosol from wood fires 1: Measurement and simulation of organic aerosol evolution. Atmos. Chem. Phys. 9, 1263–1277. https://doi.org/10.5194/acp-9-1263-2009

Kim, H., Zhang, Q., Bae, G.-N., Kim, J.Y., Lee, S.B., 2017. Sources and atmospheric processing of winter aerosols in Seoul, Korea: Insights from real-time measurements using a high-resolution aerosol mass spectrometer. Atmos. Chem. Phys. 17, 2009–2033. https://doi.org/10.5194/acp-17-2009-2017

DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, A. E., Aiken, A. C., ... & Jimenez, J. L. (2006). Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer. Analytical Chemistry, 78(24), 8281–8289. https://doi.org/10.1021/ac061249

Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., ... & Worsnop, D. R. (2015). Elemental ratio measurements of organic compounds using aerosol mass spectrometry: Improved sensitivity and intercomparability. Atmospheric Chemistry and Physics, 15(1), 253–272. https://doi.org/10.5194/acp-15-253-2015

Paatero, P., Tapper, U., 1994. Positive matrix factorization – A nonnegative factor model with optimal utilization of error estimates of data values. Environmetrics 5, 111–126. https://doi.org/10.1002/env.3170050203

Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., Jimenez, J. L., 2009. Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data. Atmos. Chem. Phys. 9, 2891–2918. https://doi.org/10.5194/acp-9-2891-2009

Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Ulbrich, I. M., Ng, N. L., Worsnop, D. R., Sun, Y., 2011. Understanding atmospheric organic aerosols via factor analysis of aerosol mass spectrometry: A review. Anal. Bioanal. Chem. 401, 3045–3067. https://doi.org/10.1007/s00216-011-5355-y

Huffman, J. A., Docherty, K. S., Aiken, A. C., Cubison, M. J., Ulbrich, I. M., DeCarlo, P. F., Jimenez, J. L., 2009. Chemically-resolved aerosol volatility measurements from two megacity field studies. Atmos. Chem. Phys. 9, 7161–7182. https://doi.org/10.5194/acp-9-7161-2009

Saha, P. K., Khlystov, A., Grieshop, A. P., 2014. Determining aerosol volatility parameters using a “dual thermodenuder” system: Application to laboratory-generated organic aerosols. Aerosol Sci. Technol. 49, 620–632. https://doi.org/10.1080/02786826.2015.1056769

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

570 Zhou, S., Collier, S., Jaffe, D. A., Briggs, N. L., Hee, J., Sedlacek III, A. J., Kleinman, L., & Lewis, K., 2017. Regional
571 influence of wildfires on aerosol chemistry in the western US and insights into atmospheric aging of biomass burning
572 organic aerosol. Atmospheric Chemistry and Physics, 17, 2477–2493. https://doi.org/10.5194/acp-17-2477-2017
573 Riipinen, I., Pierce, J. R., Donahue, N. M., Pandis, S. N., 2010. Equilibration time scales of organic aerosol inside
574 thermodenuders: Kinetics versus equilibrium thermodynamics. Atmos. Environ. 44, 597–607.
575 https://doi.org/10.1016/j.atmosenv.2009.11.022
576 Karnezi, E., Riipinen, I., Pandis, S. N., 2014. Measuring the atmospheric organic aerosol volatility distribution: a theoretical
577 analysis. Atmos. Meas. Tech. 7, 2953–2965. https://doi.org/10.5194/amt-7-2953-2014
578 Chen, Y., Wang, Z., Wang, Y., Zheng, X., Fu, P., Kawamura, K., Zhang, Y., 2021. Characterization of nitrogen-containing
579 organic aerosol in Guangzhou, China: seasonal variation, formation mechanism and source apportionment. Atmos. Chem.
580 Phys. 21, 4329–4344. https://doi.org/10.5194/acp-21-4329-2021
581 Hayes, P. L., Ortega, A. M., Cubison, M. J., Froyd, K. D., Zhao, Y., Cliff, S. S., ... Jimenez, J. L., 2013. Organic aerosol
582 composition and sources in Pasadena, California, during the 2010 CalNex campaign. J. Geophys. Res. Atmos. 118, 9233–
583 9257. https://doi.org/10.1002/jgrd.50530
584 Sun, Y., Jiang, Q., Wang, Z., Fu, P., Li, J., Yang, T., Yin, Y., 2011. Investigation of the sources and evolution processes of
585 severe haze pollution in Beijing in January 2013. J. Geophys. Res. Atmos. 119, 4380–4398.
586 https://doi.org/10.1002/2014JD021641
587 Baek, K. M., Park, E. H., Kang, H., Ji, M. J., Park, H. M., & Kim, Y. P., 2022. Seasonal characteristics of atmospheric water-
588 soluble organic nitrogen in PM2.5 in Seoul, Korea: Source and atmospheric processes of free amino acids and aliphatic
589 amines. Science of the Total Environment, 807, 150785. https://doi.org/10.1016/j.scitotenv.2021.150785
590 Milic, A., Hopke, P. K., McWhinney, R. D., Thomson, E. M., Healy, R. M., 2016. Impact of relative humidity on amine and
591 aminium salt aerosol formation from atmospheric reactions. Atmos. Chem. Phys. 16, 14527–14543.
592 https://doi.org/10.5194/acp-16-14527-2016
593 Ge, X., Wexler, A. S., Clegg, S. L., 2011. Atmospheric amines – Part I. A review. Atmos. Environ. 45, 524–546.
594 https://doi.org/10.1016/j.atmosenv.2010.10.012
595 Poste, A. E., Grung, M., & Wright, R. F. 2014. Amines and amine-related compounds in surface waters: A review of sources,
596 concentrations and aquatic toxicity. Science of the Total Environment, 487, 122–135.
597 https://doi.org/10.1016/j.scitotenv.2014.03.113
598 He, J., Liu, H., Shan, P., Zhang, K., Qin, Y., & Liu, L. 2016. Supported-gas-membrane process for removal and recovery of
599 aliphatic amines from aqueous streams. Chemical Engineering Science, 144, 110–119.
600 https://doi.org/10.1016/j.ces.2016.01.018
601 You, Y., Renbaum-Wolff, L., Carreras-Sospedra, M., Dabdub, D., Bertram, A. K., Martin, S. T., et al., 2014. Images reveal
602 that amines promote the heterogeneous reaction of epoxides in model organic aerosols. J. Phys. Chem. Lett. 5, 3211–
603 3215. https://doi.org/10.1021/jz501268k

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

Yao, L., Wang, M. Y., Wang, X. K., Zhang, W. Q., Liu, Y., Li, L., et al., 2016. Atmospheric new particle formation from sulfuric acid and amines in a Chinese megacity. Sci. Bull. 61, 939–945. https://doi.org/10.1007/s11434-016-1083-0

Kim, H., Zhang, Q., Sun, Y., Bae, G. N., Lee, B. E., Park, K., ... & Kim, Y. J. 2020. Measurement report: Characterization of severe spring haze episodes and influences of long-range transport in the Seoul metropolitan area in March 2019. Atmospheric Chemistry and Physics, 20(18), 11527–11545. https://doi.org/10.5194/acp-20-11527-2020

Jeon, J., Chen, Y., Kim, H., 2023. Influence of meteorology on emission sources and physicochemical properties of particulate matter in Seoul, Korea during heating period. Atmos. Environ. 301, 119733. https://doi.org/10.1016/j.atmosenv.2023.119733

Zhang, Q., Alfarra, M. R., Worsnop, D. R., Allan, J. D., Coe, H., Canagaratna, M. R., ... & Jimenez, J. L. 2005. Deconvolution and quantification of hydrocarbon-like and oxygenated organic aerosols based on aerosol mass spectrometry. Environmental Science & Technology, 39(13), 4938–4952. https://doi.org/10.1021/es0485681

Simoneit, B. R. T. 2002. Biomass burning – a review of organic tracers for smoke from incomplete combustion. Applied Geochemistry, 17(3), 129–162. https://doi.org/10.1016/S0883-2927(01)00061-0

Cubison, M. J., Ortega, A. M., Hayes, P. L., Farmer, D. K., Day, D., Lechner, M. J., ... & Jimenez, J. L. 2011. Effects of aging on organic aerosol from open biomass burning smoke in aircraft and laboratory studies. Atmospheric Chemistry and Physics, 11(23), 12049–12064. https://doi.org/10.5194/acp-11-12049-2011

Xu, L., Williams, L. R., Young, D. E., Allan, J. D., Coe, H., Massoli, P., Fortner, E., Chhabra, P., Herndon, S., Brooks, W. A., Jayne, J. T., Worsnop, D. R., Aiken, A. C., Liu, S., Gorkowski, K., Dubey, M. K., Fleming, Z. L., Visser, S., Prévôt, A. S. H., Ng, N. L., 2016. Wintertime aerosol chemical composition, volatility, and spatial variability in the Greater London Area. Atmos. Chem. Phys. 16, 1139–1160. https://doi.org/10.5194/acp-16-1139-2016

Feng, T., Wang, Y., Hu, W., Zhu, M., Song, W., Chen, W., ... Wang, X., 2023. Impact of aging on the sources, volatility, and viscosity of organic aerosols in Chinese outflows. Atmos. Chem. Phys. 23, 611–636. https://doi.org/10.5194/acp-23-611-2023

Scott, W. D., & Cattell, F. C. R. 1979. Vapor pressure of ammonium sulfates. Atmospheric Environment (1967), 13(6), 987–1000. https://doi.org/10.1016/0004-6981(79)90174-4

Donahue, N. M., Robinson, A. L., Pandis, S. N., 2009. Atmospheric organic particulate matter: From smoke to secondary organic aerosol. Atmos. Environ. 43, 94–106. https://doi.org/10.1016/j.atmosenv.2008.09.055

Ehn, M., Thornton, J. A., Kleist, E., Sipilä, M., Junninen, H., Pullinen, I., ... & Kulmala, M. 2014. A large source of low-volatility secondary organic aerosol. Nature, 506(7489), 476–479. https://doi.org/10.1038/nature13032

Kroll, J. H., Smith, J. D., Che, D. L., Kessler, S. H., Worsnop, D. R., Wilson, K. R., 2009. Measurement of fragmentation and functionalization pathways in the heterogeneous oxidation of oxidation organic aerosol. Environ. Sci. Technol. 43, 7826–7833. https://doi.org/10.1021/es901683r

https://doi.org/10.5194/egusphere-2025-3738
Preprint. Discussion started: 22 August 2025

636 Xu, L., Williams, L.R., Young, D.E., Allan, J.D., Coe, H., Massoli, P., Fortner, E., Chhabra, P., Herndon, S., Brooks, W.A.,
637 et al., 2016. Wintertime aerosol chemical composition, volatility, and spatial variability in the greater London area. Atmos.
638 Chem. Phys. 16, 1139–1160. https://doi.org/10.5194/acp-16-1139-2016
639 Cao, L.-M., Huang, X.-F., Li, Y.-Y., Hu, M., He, L.-Y., 2018. Volatility measurement of atmospheric submicron aerosols in
640 an urban atmosphere in southern China. Atmos. Chem. Phys. 18, 1729–1743. https://doi.org/10.5194/acp-18-1729-2018
641 Xu, W., Xie, C., Karnezi, E., Zhang, Q., Wang, J., Pandis, S.N., Ge, X., Zhang, J., An, J., Wang, Q., et al., 2019. Summertime
642 aerosol volatility measurements in Beijing, China. Atmos. Chem. Phys. 19, 10205–10216. https://doi.org/10.5194/acp-
643 19-10205-2019
644