

Photochemical Processing of Dissolved Organic Matter in Fog Water: Oxidation and Functionalization Pathways Driving Organic Aerosol Evolution

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Abstract. Photochemical reactions of dissolved organic matter (DOM) in atmospheric waters can alter the composition and properties organic aerosols (OA), with implications for climate and air quality. In this study, we investigated the aqueous-phase transformation of fog DOM under simulated sunlight using online aerosol mass spectrometry (AMS), offline Orbitrap mass spectrometry with electrospray ionization, UV-vis spectroscopy, and aerosol volatility measurements. Irradiation increased the mass concentration of DOM-derived OA (DOM_{OA}), defined as the low-volatility fraction of DOM that forms OA upon water evaporation. This increase was primarily driven by functionalization reactions that added oxygen- and nitrogen-containing groups, as indicated by a stable C mass, rising oxygen-to-carbon (O/C) and nitrogen-to-carbon (N/C) ratios, and enhanced signals of heteroatom-containing compounds over the course of irradiation. Despite evidence of fragmentation, spectral features associated with oligomerization, such as phenolic dimers, were also observed. To characterize chemical aging of fog DOM, we applied positive matrix factorization to the AMS spectra and identified three distinct factors representing progressive stages of aqueous-phase aging: initial DOM_{OA}, more oxidized intermediates, and highly oxidized products, characterized by progressively increasing O/C and N/C ratios. These findings demonstrate that sunlight-induced aqueous-phase oxidation and functionalization of fog DOM drive the formation and aging of secondary OA, altering its composition, volatility, and light-absorbing properties with potential atmospheric consequences.

1 Introduction

Dissolved organic matter (DOM) is a ubiquitous and chemically diverse component of cloud, fog, and rain droplets, where it plays a central role in the chemical and physical evolution of atmospheric aqueous systems. DOM originates from various sources, including the dissolution of soluble gases, uptake of hygroscopic particles, and multiphase oxidation of hydrophobic compounds into water-soluble forms (Bianco et al., 2020; Collett et al., 2008; Herckes et al., 2013; Kim et al., 2019; Mazzoleni

et al., 2010; Pratap et al., 2021; Schneider et al., 2017). As a result, its composition is highly complex (Bianco et al., 2018; Brege et al., 2018; Mazzoleni et al., 2010; Pailler et al., 2024; Sun et al., 2021; Zhao et al., 2013), encompassing both small polar molecules (e.g., organic acids, carbonyls, dicarbonyls, and organosulfates) (Altieri et al., 2009b; Boris et al., 2018; Herckes et al., 2002a; Liu et al., 2021; Pratt et al., 2013) and high molecular weight (HMW) species such as humic-like substances and secondary oligomers (Altieri et al., 2009b; Collett et al., 2008; Hawkins et al., 2016; Laskin et al., 2015; Renard et al., 2015; Sun et al., 2010). Primary particle tracers, such as n-alkanes, long-chain alkanolic acids, and polycyclic aromatic hydrocarbons (PAHs), have also been detected in fog and cloud droplets, though they typically represent only a minor fraction of dissolved carbon, even in heavily polluted areas (Collett et al., 2008; Ehrenhauser et al., 2012).

In addition to carbon-rich compounds, organic nitrogen (ON) and organic sulfur (OS) species are also prevalent in atmospheric waters. These include amines, N-containing heteroaromatics, nitrophenols, and nitrooxy-organosulfates (Altieri et al., 2009a; Desyaterik et al., 2013; Kim et al., 2019; Mattsson et al., 2025; Sun et al., 2024; Youn et al., 2015; Zhang et al., 2002; Zhang and Anastasio, 2003b), particularly in regions impacted by biomass burning and agricultural emissions (Collett et al., 2008; Li et al., 2023; Mattsson et al., 2025; Parworth et al., 2017; Zhang and Anastasio, 2001). ON and OS species can enter cloud and fog droplets via direct uptake of gaseous or particulate species, or they may form secondarily through aqueous-phase reactions involving precursors such as ammonia, amines, amino acids, and SO₂.

A wide range of VOCs (e.g., isoprene, monoterpenes, glyoxal, methylglyoxal, and phenols) contribute to DOM via gas-to-liquid partitioning followed by aqueous-phase reactions (Arciva et al., 2022; Ervens et al., 2008; Jiang et al., 2021; Tomaz et al., 2018; Wang et al., 2021; Yu et al., 2014; Zhang et al., 2024). These VOCs, along with pre-existing DOM, can undergo direct photolysis or react with a suite of oxidants, including hydroxyl radical ($\bullet\text{OH}$), singlet oxygen ($^1\text{O}_2^*$), hydrogen peroxide, peroxy radicals, ozone (O₃), nitrate radical ($\bullet\text{NO}_3$), sulfate radical ($\bullet\text{SO}_4^-$), and organic triplet excited states ($^3\text{C}^*$) (Bianco et al., 2020; Borduas-Dedekind et al., 2019; Hems et al., 2020; Herrmann et al., 2015; Jiang et al., 2023; Kaur et al., 2019; Smith et al., 2015; Tomaz et al., 2018; Zhang and Anastasio, 2003a). These reactions significantly alter the aqueous phase composition and, following droplet evaporation, influence the concentration, oxidation state (OS_C), and molecular makeup of the resulting organic aerosols (OA) (Farley et al., 2023; Hems et al., 2020; Kim et al., 2019; Lee et al., 2012; Renard et al., 2015; Schneider et al., 2017; Schurman et al., 2018). Consequently, aqueous-phase processing of DOM affects OA's light absorption and cloud activation properties, with broad implications for atmospheric chemistry and Earth's radiative budget (Borduas-Dedekind et al., 2019; Farley et al., 2023; Hems et al., 2020).

Despite growing recognition of the importance of aqueous-phase chemistry, significant knowledge gaps remain regarding the evolution of real-world DOM under ambient atmospheric conditions. These uncertainties limit our ability to predict aerosol-cloud interactions, which represent one of the largest sources of uncertainty in climate models. While laboratory studies have yielded valuable mechanistic insights, they often rely on simplified model systems that don't capture the chemical complexity of ambient DOM. Other studies using real-world samples often employed non-atmospheric irradiation (e.g., 254 nm UV), reducing their relevance to atmospheric processes.

65 In this study, we examine the photochemical transformation of DOM in wintertime fog water collected in Fresno, California
– a major urban center in the San Joaquin Valley (SJV), where fog plays a key role in winter aerosol pollution. The SJV has
been the subject of extensive fog chemistry research (Collett et al., 2001; Collier et al., 2018; Ehrenhauser et al., 2012; Ge et
al., 2012a; Herckes et al., 2015; Kim et al., 2019; Zhang and Anastasio, 2001), and Fresno fog water is known to contain a
complex mixture of organic compounds spanning a wide range of chemical properties (Herckes et al., 2007; Kim et al., 2019;
70 Mazzoleni et al., 2010; Zhang and Anastasio, 2001). Here, we define “DOM” as the total pool of dissolved organics, including
water-soluble gases, and “DOM_{OA}” as the low-volatility fraction that remains in the particle phase after fog water
aerosolization and drying. We used a high-resolution time-of-flight aerosol mass spectrometer (HR-AMS) to track DOM_{OA}
concentration and composition in real time during simulated sunlight illumination. Positive matrix factorization (PMF) was
applied to the HR-AMS spectra to resolve distinct stages of aqueous-phase aging, complemented by molecular analysis using
75 Orbitrap mass spectrometry with electrospray ionization (ESI-MS), UV-Vis spectroscopy, and thermodenuder measurements
of aerosol volatility.

2 Experimental methods

2.1 Collection of fog water samples

The fog water samples were collected on Jan 9, 2010, in Fresno in the SJV of California, as detailed in Kim et al. (Kim et al.,
80 2019). The sampling site was situated at a large agricultural field of California State University, Fresno (36°49'35.9"N,
119°44'42.7"W), in relatively close proximity to two major highways and a residential area (Ehrenhauser et al., 2012; Wang
et al., 2013). Fog samples were collected using Caltech Active Strand Cloud Collectors (CASCC; ~ 25.4 m³ min⁻¹ airflow)
(Demos et al., 1996) and a stainless steel extra-large CASCC collector (XL-CASS; ~ 40 m³ min⁻¹ air flow) (Herckes et al.,
2007). All samples were immediately filtered onsite using 0.22 µm glass fiber filters (Wang et al., 2013) and stored in the dark
85 at –20 °C until use. The characteristics of the fog samples have been reported by Kim et al. (2019) and are summarized in
Table S1. Three consecutive fog samples with highly similar chemical composition were combined to yield approximately
110 mL of composite sample, the volume required for photooxidation experiments conducted in February 2015. Although
multiyear storage can potentially affect certain labile compounds, these samples were also analyzed shortly after collection,
and the results were reported previously (Kim et al., 2019). The HR-AMS spectrum of the unilluminated fog sample from this
90 study is highly similar to the spectra reported by Kim et al. (2019), indicating that DOM_{OA} composition remained largely
unchanged during storage. Additionally, the composition of the fog samples used in this study is also similar to other winter
fog water samples from Fresno (Kim et al., 2019) and from Davis, CA, indicating their representativeness for winter fogs in
California's Central Valley.

Aqueous oxidation was carried out using air-saturated fog water stirred in a Pyrex tube and exposed to simulated sunlight inside an RPR-200 Photoreactor System equipped with three types of bulbs emitting wavelengths of light centered at 300, 350 and 419 nm, respectively. Fig. S1 shows the normalized photon fluxes inside the RPR-200 illumination system. In this setup, lamp emission below 315 nm is minimal, and the Pyrex tube further blocks wavelengths below 300 nm, effectively confining the actinic flux reaching the solution to the UVA and visible range. No additional optical filters were employed. Prior actinometry measurements of this RPR-200 illumination system indicate that its photochemical rate is ~ 7 times faster than that of winter solstice midday sunlight in Northern California (George et al., 2015). Accordingly, the ~ 8 h of illumination applied in our photochemical experiments corresponds to approximately 56 h of exposure to ambient sunlight. Under this condition, a variety of oxidants, such as hydroxyl radical ($\bullet\text{OH}$), nitrate radical ($\bullet\text{NO}_3$), triplet states of organic carbon ($^3\text{C}^*$), and singlet molecular oxygen ($^1\text{O}_2^*$), can be produced during illumination and react with dissolved organics in the aqueous phase. $^3\text{C}^*$ can form when brown carbon chromophores in fog water absorb light and undergo intersystem crossing (McNeill and Canonica, 2016). Energy transfer between $^3\text{C}^*$ and dissolved O_2 yields $^1\text{O}_2^*$ (Kaur and Anastasio, 2017; Ossola et al., 2021). H_2O_2 can be generated via energy/electron transfer of $^3\text{C}^*$ (Anastasio et al., 1997), which can subsequently undergo photolysis to produce $\bullet\text{OH}$. Additionally, $\bullet\text{OH}$ can be generated from nitrate and nitrite photolysis in fog water (Brezonik and Fulkerson-Brekken, 1998). Previous studies have reported steady-state $\bullet\text{OH}$ concentration in fog water from Northern California (winter sunlight) in the range of $3.4\text{--}6.6 \times 10^{-16}$ M, and $^1\text{O}_2^*$ concentration of $1.1\text{--}6.1 \times 10^{-13}$ M (Anastasio and McGregor, 2001). A Shimadzu LC-10AD high-performance liquid chromatography pump continuously drew solution at a flow rate of 0.2 mL min^{-1} from the illuminated tube or a dark control tube wrapped entirely with aluminum foil. The effluent was atomized with nitrogen, fully dried using a diffusion dryer, and analyzed in real-time by HR-AMS. The non-refractory organics detected after this atomization-drying process are defined as DOM_{OA} , while compounds that completely volatilize during drying are not included. This nebulizer-dryer-AMS approach has been widely used in prior fog studies (Brege et al., 2018; Kim et al., 2019; Mattsson et al., 2025). The illuminated solution was continuously aerosolized and sampled until fully consumed, which took ~ 8 hours. Additionally, aliquots of the illuminated fog water samples were collected over four consecutive time intervals (S1: 0–2 h, S2: 2–4 h, S3: 4–6 h, and S4: 6–8 h) and analyzed offline by electrospray ionization mass spectrometry (ESI-MS) and UV-vis spectroscopy.

2.3 HR-AMS measurement and data analysis

2.3.1 HR-AMS measurement and data analysis

Bulk chemical composition and elemental ratios of DOM_{OA} were analyzed using the HR-AMS, which employs 70 eV electron ionization (EI) mass spectrometry after aerosol evaporation at $\sim 600^\circ\text{C}$ (DeCarlo et al., 2006). The instrument was operated in both “V” and “W” ion optical modes, achieving mass resolutions of ~ 3000 and ~ 5000 , and capturing spectra up to m/z 500 and 300 amu, respectively.

HR-AMS data were processed using SQUIRREL v1.15 and PIKA v1.56 (available at <http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/>). W-mode data were used to obtain high-resolution mass spectra (HRMS) and derive elemental ratios, including oxygen-to-carbon (O/C), hydrogen-to-carbon (H/C), nitrogen-to-carbon (N/C), sulfur-to-carbon (S/C), and the organic mass-to-carbon ratio (OM/OC) (Aiken et al., 2008). With relative humidity at the HR-AMS inlet below 5%, contributions from water vapor were considered negligible, and the organic H_2O^+ signal was estimated by subtracting the sulfate-derived contribution from the total H_2O^+ signal (Allan et al., 2004). To estimate the organic CO^+ signal, we performed a separate, offline HR-AMS analysis of fog samples using argon as the atomization gas (Yu et al., 2014), which eliminates the interference from N_2 at m/z 28. The argon-atomized measurements showed that the CO^+ signal was $\sim 31\%$ as intense as the CO_2^+ signal in DOM_{OA} mass spectra. This ratio ($\text{CO}^+ = 0.31 \times \text{CO}_2^+$) was then applied to the online N_2 -atomized HR-AMS data to improve the accuracy of DOM_{OA} O/C and OM/OC estimates.

2.3.2 Positive Matrix Factorization (PMF) analysis

PMF analysis was performed using the PMF2.exe algorithm in robust mode (Paatero and Tapper, 1994), via the PMF Evaluation Toolkit (PET) v2.06 (Ulbrich et al., 2009), available at http://cires.colorado.edu/jimenez-group/wiki/index.php/PMF-AMS_Analysis_Guide. The input data included the ion-speciated HRMS matrix (containing 287 ions and 1001 time points) and its corresponding error matrix, prepared following the refinement protocol outlined in Table 1 of Zhang et al. (Zhang et al., 2011).

To identify the optimal solution, PMF was run using factor numbers (p) from 1 to 5 and rotational parameters ($fPeak$) from -1.0 to 1.0 in 0.1 increment, as recommended by Zhang et al. (Zhang et al., 2011). After a thorough examination, the 3-factor solution with $fPeak = -0.1$ ($Q/Q_{exp} = 5.57$) was chosen. A summary of key diagnostic plots is presented in Fig. S2 in the supplementary materials. This solution best captured both the total DOM_{OA} mass and its temporal evolution (Fig. S2f), with only minor variations across different $fPeak$ values (Fig. S2c). For comparison, the 2-factor and 4-factor solutions are shown in Fig. S3, with diagnostics in Figs. S4–S5. The 2-factor solution underperformed during the initial irradiation phase, while the 4-factor solution split one interpretable component into two less meaningful factors. Overall, the 3-factor solution provided the most robust and interpretable description of DOM_{OA} evolution under simulated sunlight.

2.4 Determination of DOM_{OA} formation and decay rates for the three PMF factors

The formation and decay kinetics of DOM_{OA} associated with the three PMF factors were determined through curve fitting using Igor Pro 6.36 (Wavemetrics, Portland, OR, USA). The temporal evolution of each factor was modelled using exponential functions. The decay of Factor 1 was fitted using a pseudo first-order kinetic model:

$$[\text{DOM}_{\text{OA-fac1}}]_t = a + b \cdot \exp(-k_d t) \quad (1)$$

For Factor 2, both formation and decay processes were considered and modeled using a double exponential function:

$$[\text{DOM}_{\text{OA-fac2}}]_t = a + b \cdot \exp(-k_f t) + c \cdot \exp(-k_d t) \quad (2)$$

The formation rate of Factor 3 was modeled as a first-order process driven by the decay of Factor 2:

$$[\text{DOM}_{\text{OA-fac3}}]_t = a + b \cdot \exp(-k_f t) \quad (3)$$

160 Here, $[\text{DOM}_{\text{OA-fac}i}]_t$ is the concentration of the i -th DOM_{OA} factor at time t ; a , b , and c are fitted coefficients; k_f and k_d represent apparent first-order formation and decay rate constants, respectively. These parameters were obtained by least-squares fitting the models to the experimental data.

2.5 ESI-MS analysis

165 Fog water samples collected over four irradiation time intervals, corresponding to distinct photochemical aging stages (Fig. S6), were analyzed using an LTQ Orbitrap mass spectrometer (Thermo Scientific, Inc.) equipped with an electrospray ionization (ESI) source operated in positive mode for molecular characterization. Winter fog DOM in Fresno is characterized by high N/C ratios and elevated concentrations of N-containing organics, such as amines, amino acids and imidazoles (Kim et al., 2019), which are protonatable and exhibit strong sensitivity in positive-mode ESI. Given our interest in formation and transformation of organic nitrogen species, we analyzed the samples in positive mode. Mass spectrometry data were acquired using Xcalibur software, and individual MS peaks with signal-to-noise ratio (S/N) > 10 were extracted using the Decon2LS program. Subsequent processing and formula assignments were conducted with customized Microsoft Excel macros (Roach et al., 2011) based on Kendrick mass (KM) defect analysis with a KM base of CH_2 , excluding ^{13}C isotopes. Formula assignments were restricted by a mass accuracy threshold of < 5 ppm and the following elemental limits: $\text{C} \leq 100$, $\text{H} \leq 200$, $\text{O} \leq 50$, $\text{N} \leq 4$, $\text{S} \leq 2$, and $\text{Na} \leq 1$. Elemental ratios were confined to $0.0 \leq \text{H/C} \leq 3.0$ and $0.0 \leq \text{O/C} \leq 3.0$. The formulas of neutral species were subsequently determined by removing the adducting ions (e.g., H^+ or Na^+).
175

3. Results and discussion

3.1 Photochemical transformation of low-volatility organic species in fog water

180 Photochemical processing significantly altered the mass concentration and chemical composition of low-volatility organic solutes (DOM_{OA}) in fog water. As shown in Figs. 1d and S7, DOM_{OA} increased from 25% to 38% of total solute mass over ~ 8 hours of simulated sunlight exposure – equivalent to roughly 56 hours of winter solstice midday sunlight in Northern California based on actinometry measurements (George et al., 2015). In contrast, major inorganic species (i.e., nitrate, ammonia, sulfate, and chloride) remained largely unchanged, indicating net production of low-volatility organic compounds via aqueous-phase photochemistry.

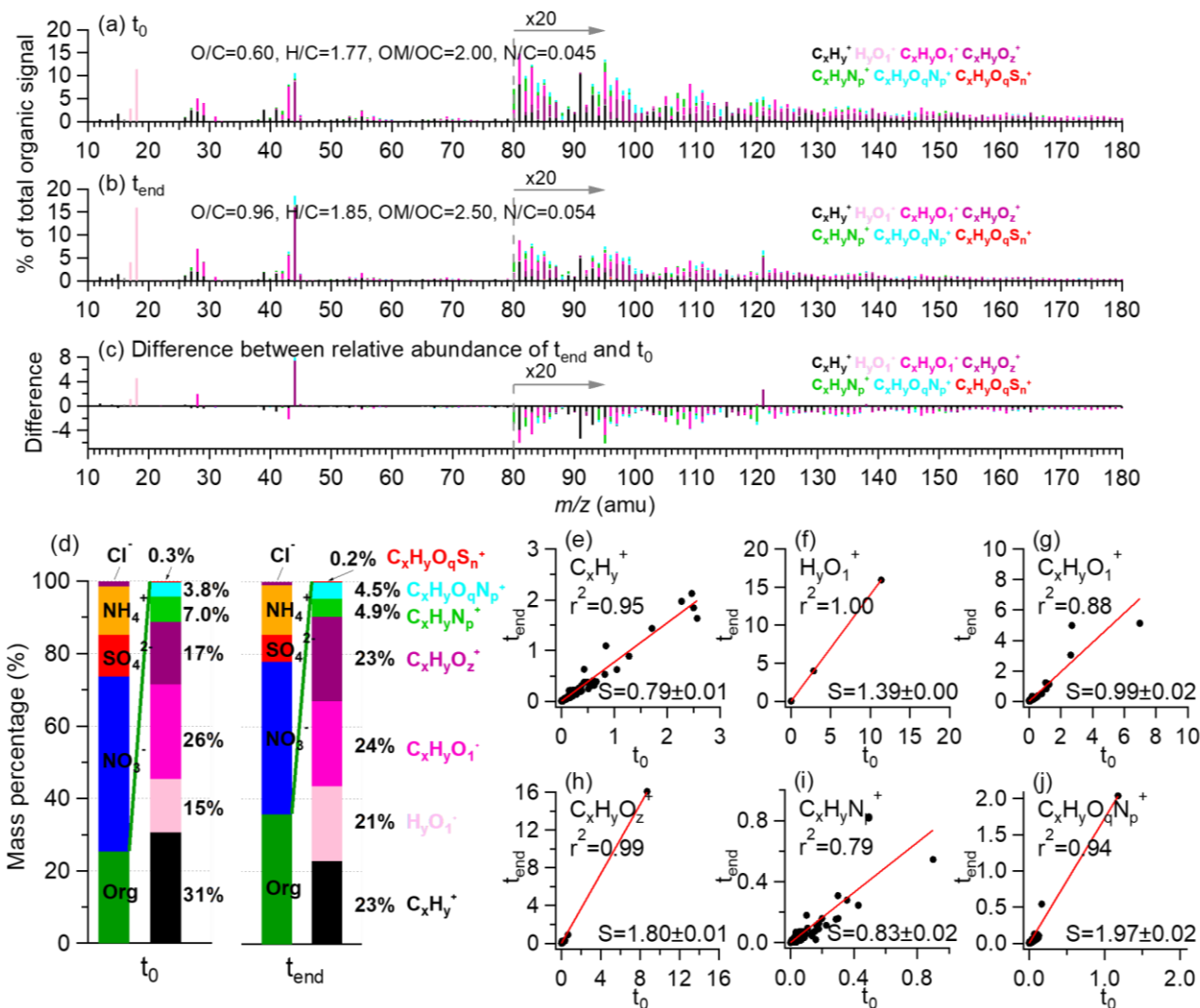


Figure 1. Overview of DOM_{OA} composition before (t_0) and after (t_{end}) eight hours of simulated sunlight illumination. (a-c) HR-AMS spectra of DOM_{OA} at t_0 and t_{end} , and the difference spectrum between them (t_{end} minus t_0), with peaks color-coded by ion categories: $C_xH_y^+$, $H_yO_1^+$, $C_xH_yO_1^+$, $C_xH_yO_2^+$, $C_xH_yN_p^+$, $C_xH_yO_qN_p^+$, $C_xH_yO_qS_n^+$ ($x \geq 1$; $y \geq 1$; $z \geq 1$; $p \geq 1$; $q \geq 1$; $n \geq 1$). Signals at $m/z \geq 80$ are multiplied by 20 for clarity. Elemental ratios are noted in the legend. (d) Mass fractions of major inorganic species and DOM_{OA} ion categories at t_0 and t_{end} (colors of ion categories match panels a-c). (e-j) Comparison of each ion category's signal contributions (% of total organic signal) at t_0 and t_{end} . Red lines show orthogonal distance regression (ODR) fits; slopes (S) and correlation coefficients (r^2) are provided in each panel.

Irradiation-induced changes in DOM_{OA} composition are evident in the HR-AMS spectra (Figs. 1a-c). The O/C ratio increased from 0.60 prior to illumination (t_0) to 0.96 at t_{end} , and the fraction of CO_2^+ to total organic signal ($f_{CO_2^+}$) increased from 8.5% to 15.5%, reflecting substantial oxidative aging processes. These changes are consistent with ambient wintertime observations in Fresno using real-time HR-AMS (Chen et al., 2018; Young et al., 2016). DOM_{OA} at t_0 resembled less-oxidized oxygenated OA (LO-OOA) and semi-volatile OOA (SV-OOA), while after irradiation it was more similar to more-oxidized OOA (MO-

OOA) and low-volatility OOA (LV-OOA) (Figs. 2d and S8). SV-OOA and LV-OOA are typically representative of relatively fresh and more-aged SOA, respectively (Ng et al., 2010). In addition, the nitrogen-to-carbon (N/C) ratio of DOM_{OA} increased from 0.045 to 0.054, indicating incorporation of nitrogen into the organic matrix, likely through reactions between DOM and N-containing nucleophiles such as ammonia, amino acids, and amines (Haan et al., 2009; Hawkins et al., 2016; Nozière et al., 2009; Shapiro et al., 2009). The AMS NO₂⁺/NO⁺ ratio decreased from 1.37 to 0.72 during illumination (Fig. S9), consistent with formation of low-volatility organic nitrates (Day et al., 2022; Farmer et al., 2010).

Figures 1e-j show scatter plots comparing the contributions of major HR-AMS ion families (i.e., C_xH_y⁺, H_yO₁⁺, C_xH_yO₁⁺, C_xH_yO_z⁺, C_xH_yN_p⁺, and C_xH_yO_qN_p⁺ (x ≥ 1; y ≥ 1; z > 1; p ≥ 1; q ≥ 1)) to the total organic signal at t₀ and t_{end}. The corresponding comparisons of absolute ion signals are shown in Figure S10. In most cases, orthogonal distance regression (ODR) slopes (S) significantly deviated from unity, highlighting systematic chemical evolution of DOM_{OA} during irradiation. The decreases of hydrocarbon-like ions (C_xH_y⁺, S = 0.79; Fig. 1e) suggest fragmentation of carbon backbones via photooxidation. In HR-AMS, organic-derived H_yO₁⁺ ions are generated during vaporization and ionization of oxygenated organics such as carboxylic acids and alcohols (Canagaratna et al., 2015). In Fig. 1f, H_yO₁⁺ ions showed a slope of 1.39, suggesting formation of oxygenated organics. The overall fractional contribution of the lightly oxygenated ion family (C_xH_yO₁⁺) remained unchanged during illumination (S=0.99; Fig. 1g). However, several individual ions departed significantly from the 1:1 line, indicating compositional change within the family. In contrast, the relative abundance of more oxygenated ions (C_xH_yO_z⁺; Fig. 1h) increased sharply (S = 1.80), and their tightly correlated spectral patterns at t₀ and t_{end} (r² = 0.99) suggest formation of highly oxidized species with structural similarity to pre-existing compounds. The dominance of CO₂⁺ and CHO₂⁺ within this family suggests carboxylation as a major pathway. In parallel, reduced organic nitrogen ions (C_xH_yN_p⁺; Fig. 1i) decreased in relative abundance (S = 0.83), while oxidized organic nitrogen ions (C_xH_yO_qN_p⁺; Fig. 1j) increased (S = 1.97). Consequently, the C_xH_yN_p⁺/C_xH_yO_qN_p⁺ ratio decreased from 2.1 to 1.2 (Fig. S11), consistent with oxidative transformation and functionalization of ON species during aqueous-phase processing.

Figure 2 illustrates the temporal evolution of DOM_{OA} during irradiation. Its mass concentration increased steadily (Fig. 2a), accompanied by rising O/C and N/C ratios, indicating continuous photochemical transformation. Despite these changes, the total carbon concentration remained nearly constant over 8 hours of irradiation (RSD = 1.3%, Fig. 2a), suggesting minimal carbon loss to the gas phase. While previous studies have reported that ~ 10% of dissolved organic carbon in fog can be small volatiles such as acetate, formate, and formaldehyde (Herckes et al., 2002b), such VOCs were not detected in our samples (Kim et al., 2019). Although some volatilization during storage is possible, samples were stored in sealed containers at -20 °C in the dark, minimizing reaction losses. As shown in Fig. 2a, the observed DOM_{OA} mass increase was primarily driven by oxygen incorporation, with nitrogen addition playing a lesser role.

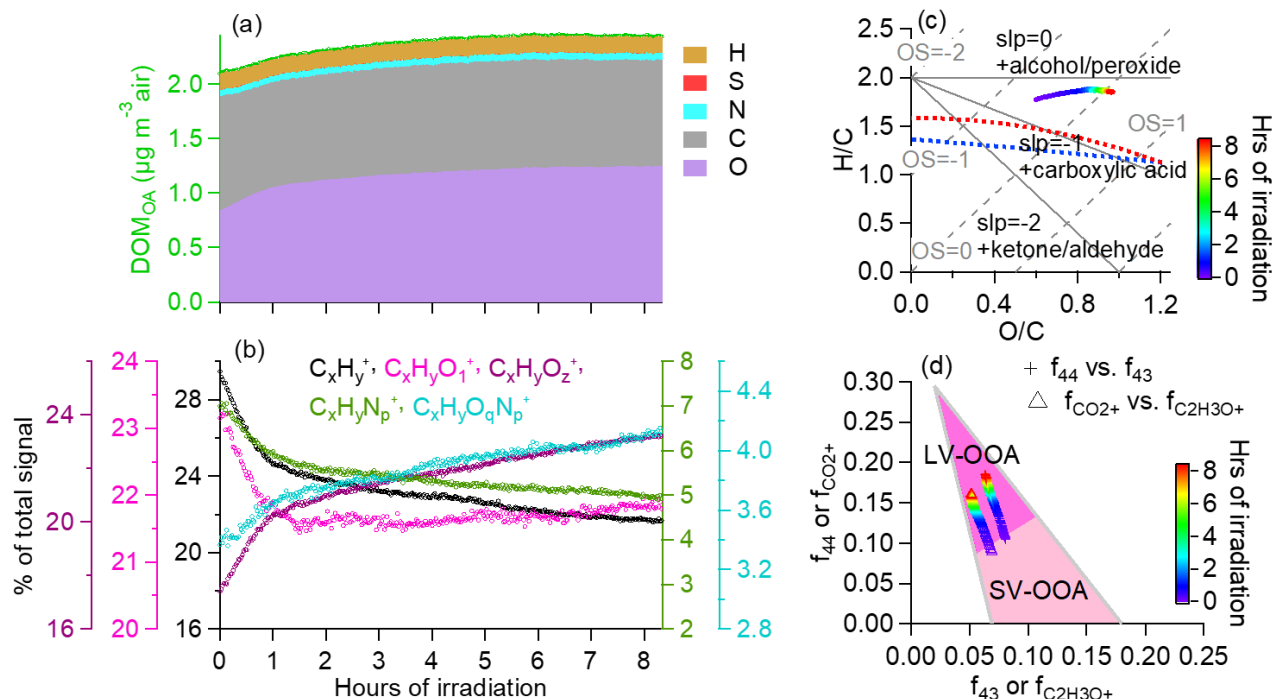


Figure 2. Time evolution of DOM_{OA} composition during simulated sunlight illumination. (a) DOM_{OA} concentration and stacked mass contributions from O, C, N, S and H atoms. The mass concentrations represent ambient air concentrations, calculated by normalizing the liquid-phase concentrations to the sampled air volumes. (b) Fractional contributions of major ion categories to the total DOM_{OA} signals in HR-AMS spectra: $C_xH_y^+$, $C_xH_yO_1^+$, $C_xH_yO_z^+$, $C_xH_yN_p^+$, and $C_xH_yO_qN_p^+$ ($x \geq 1$; $y \geq 1$; $z \geq 1$; $p \geq 1$; $q \geq 1$). (c) Evolution profiles of DOM_{OA} in Van Krevelen space based on AMS measurements. (d) Evolution of f_{44} (fraction of m/z 44 in the AMS organic spectrum), f_{43} (fraction of m/z 43), $f_{CO_2^+}$ (fraction of CO_2^+ ion) and $f_{C_2H_3O^+}$ (fraction of $C_2H_3O^+$ ion). In this study, CO_2^+ dominates m/z 44 (83%-88%), with minor contributions from $C_2H_6N^+$ and CH_2NO^+ . $C_2H_3O^+$ dominates m/z 43, with $C_3H_7^+$, $C_2H_5N^+$, and $CHNO^+$ contributing the remainder. The shaded triangle area denotes the region where most ambient oxygenated organic aerosol (OOA) falls into, with the upper-right corner characteristic of low-volatility OOA (LV-OOA) and the lower-right corner of semi-volatile OOA (SV-OOA) (Ng et al., 2010, 2011).

Figures 2b and S12 provide further insights into the photochemical evolution of DOM_{OA} through temporal trends and correlation analysis of five major HR-AMS ion categories. Signals from less oxygenated species ($C_xH_y^+$, $C_xH_yO_1^+$ and $C_xH_yN_p^+$) decreased in their contribution to the total organic signal with irradiation, while more oxidized and nitrogen-functionalized categories ($C_xH_yO_z^+$ and $C_xH_yO_qN_p^+$) increased, indicating progressive oxidation and nitrogen incorporation. The decline in $C_xH_y^+$ reflects the breakdown of aliphatic and aromatic precursors, while the rise in $C_xH_yO_z^+$ and $C_xH_yO_qN_p^+$ is consistent with enhanced oxygenation and functionalization.

Strong negative correlations between $C_xH_y^+$ and both $C_xH_yO_z^+$ and $C_xH_yO_qN_p^+$ support the conversion of less oxidized compounds into highly oxygenated species. Additionally, positive correlations among O- and N-containing ions suggest shared aqueous-phase formation pathways, potentially involving reactions with nitrogenous species such as ammonium, amines, or organic nitrates. Collectively, these results highlight the extensive molecular transformation of DOM_{OA} during photochemical

aging, involving both functionalization and fragmentation, with a net buildup of highly functionalized organics. The evolving HR-AMS ion signatures are consistent with the aqueous-phase formation of SOA-like material under atmospheric conditions.

250 3.2 Insights into photochemical aging pathways of fog DOM

Photochemical aging of fog DOM involves both fragmentation of high-molecular-weight compounds and formation of highly functionalized, O- and N-containing species, as revealed by complementary ESI-MS and HR-AMS analyses.

255 Molecular-level insights from positive-mode ESI-MS corroborated the HR-AMS findings. As shown in Fig. S13, the relative abundance of CHN compounds decreased from 7.3% to 3.7% over 8 hours of irradiation, while the CHONS compounds increased from 27.4% to 39.5%. The total CHON fraction remained relatively stable (38.9%–40%), but individual compounds, such as $C_9H_{17}NO_8$, increased markedly (Fig. 3a), suggesting oxidative conversion of CHN species (e.g., amines, imines, and heterocyclics) into more oxidized forms. The CHN species that decreased during irradiation were primarily $C_7 - C_{16}$ compounds (Fig. 3c), whereas the CHON increases were mainly driven by C_9 species and the CHONS increases were associated with smaller molecules (e.g., C_2 , C_3 , C_4 , and C_{11}) (Figs. 3f & 3h). These shifts in carbon number indicate
260 fragmentation pathways that produce smaller O-, N-, and S-containing products.

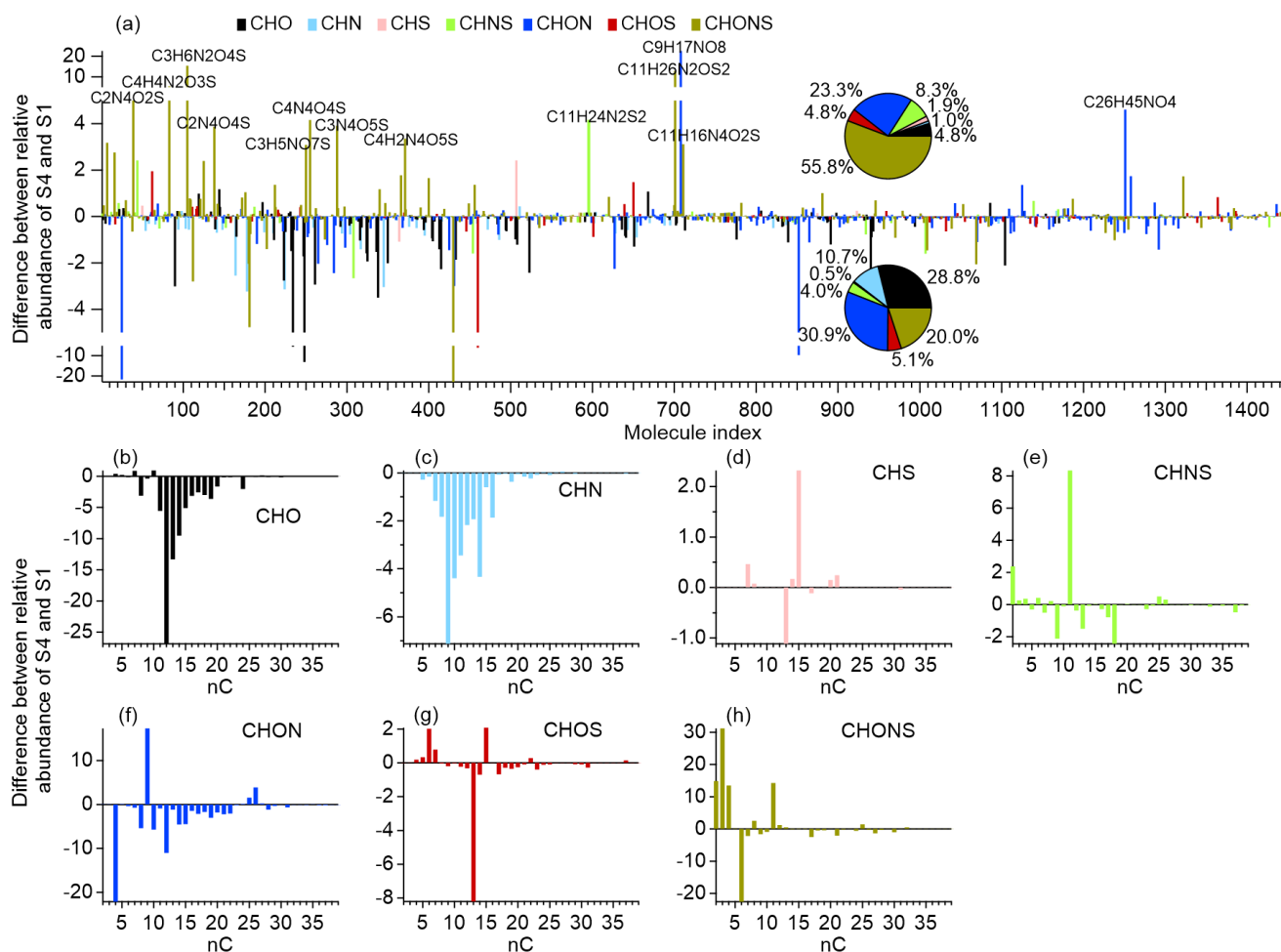


Figure 3. Compositional changes in fog DOM observed by positive-mode ESI-MS between the early (0–2 h, S1) and late (6–8 h, S4) irradiation periods. (a) Difference in relative abundance of all detected molecular formulas between S1 and S4; (b–h) Histograms showing changes in relative abundance of compounds grouped by carbon number for each molecular class: CHO, CHN, CHS, CHNS, CHON, CHOS, and CHONS.

Fragmentation was also evident in HR-AMS data, with high-mass ion signals declining after irradiation. As shown in Figure 4, the unit mass resolution (UMR) spectra of DOM_{OA} in the m/z 180–450 range showed widespread signal reductions consistent with the breakdown of HMW species known to present in fog water (Ehrenhauser et al., 2012; Herckes et al., 2002b; Mazzoleni et al., 2010). However, a set of peaks (e.g., m/z 214, 230, 258, 275, 334, and 350) increased in intensity, with some spaced by 16 amu – indicative of progressive oxygen addition through reactions such as hydroxylation, peroxide formation, or radical-mediated reactions. This interpretation is also supported by the evolution of H/C and O/C ratios in Van Krevelen space (Fig. 2c), which follows a near-zero slope, consistent with net oxygen incorporation. Additionally, the fractional contribution of CHO₂⁺ to the total organic signal gradually increased from 0.63% to 0.93% during irradiation (Fig. S14), suggesting that carboxylation played an important role in the formation of functionalized products. High-resolution peak fitting of these

increased ions indicates that they either contain nitrogen or consist solely of C, H and O (Fig. S15). These results imply that photochemical aging of fog DOM involves both loss of HMW compounds and formation of new functionalized products.

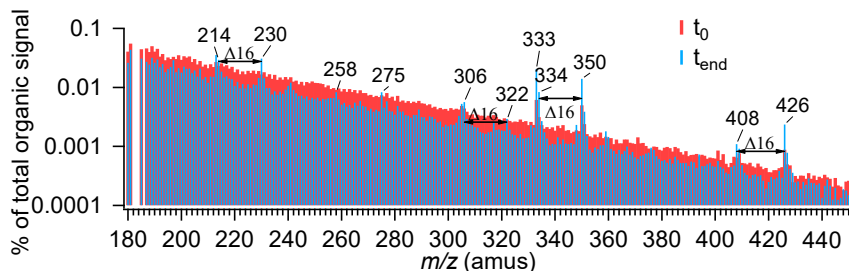


Figure 4. Comparison of unit mass resolution (UMR) spectra of DOM_{OA} in fog water before (t_0 , blue) and after (t_{end} , red) simulated sunlight illumination, over the m/z range 180–450 amu.

Notably, the m/z 306 signal, a known tracer ion for syringol dimer formation (Sun et al., 2010; Yu et al., 2014), was enhanced following irradiation. Syringol, a methoxyphenol commonly emitted during biomass burning, is likely present in the fog water due to winter residential wood burning in the region (Chen et al., 2018; Ge et al., 2012b; Young et al., 2016). The enhancement of m/z 306 provides direct evidence of aqueous-phase oligomerization of biomass burning-derived phenolic precursors, consistent with prior laboratory (Huang et al., 2018; Jiang et al., 2021, 2023; Yu et al., 2016) and field studies showing photooxidation of phenolics leads to hydroxylation, ether formation, and oligomerization (Gilardoni et al., 2016).

Together, these findings highlight the dual role of aqueous-phase photochemistry: simultaneous fragmentation of existing DOM and generation of new, more oxygenated species with enhanced functionality. The concurrent increases in oxidation and nitrogen incorporation are consistent with aqueous-phase aging pathways that produce SOA-like material enriched in O- and N-functional groups.

3.3 Characterizing aqueous phase photoaging of DOM_{OA} via PMF

We applied PMF to the HR-AMS spectra to further resolve the progressive aqueous-phase aging of DOM_{OA} during simulated sunlight irradiation. This analysis allows us to deconvolve overlapping transformation processes and link them to chemical composition and reactivity. Three distinct factors were identified (Fig. 5), each corresponding to a different stage of photochemical processing. Factor 1 represented the initial DOM_{OA}, characterized by O/C = 0.66, H/C = 1.82, OS_C = -0.5, and N/C of 0.036. Its mass spectrum closely matched that of the bulk DOM_{OA} at t_0 . This factor decayed rapidly, with a first-order loss rate constant of $k_d = 2.0 \text{ hr}^{-1}$. Factor 2 emerged shortly after the start of illumination and peaked around 1.5 hours, increasing with a formation rate constant of $k_f = 2.6 \text{ hr}^{-1}$ before gradually declining at $k_d = 0.016 \text{ hr}^{-1}$. This intermediate factor exhibited increased oxidation (O/C = 0.96) and a slightly higher N/C (= 0.038) compared to Factor 1, indicating the incorporation of oxygenated functional groups into DOM. The transient nature and intermediate oxidation level of Factor 2 imply that it represented a key transformation stage, where precursor molecules were actively undergoing aqueous-phase reactions, likely including hydroxylation, carbonyl formation, and nitrogenation (Hawkins et al., 2016; Herrmann et al., 2015; Renard et al., 2015), on their way to forming more stable, low-volatility products.

Factor 3, the most oxidized component with the highest O/C (1.12) and N/C (0.040) ratios, accumulated gradually throughout the irradiation period, with an estimated formation rate constant of $k_f = 0.13 \text{ hr}^{-1}$. This factor was enriched in highly oxygenated fragments (e.g., $\text{C}_x\text{H}_y\text{O}_z^+$), including ions such as CO_2^+ and CHO_2^+ , which are markers for carboxylic acids and other highly oxidized organic compounds. The elevated N/C ratio of Factor 3 (0.040 vs. 0.036 for Factor 1) indicates nitrogen incorporation into DOM_{OA} during photochemical aging. This conclusion is supported by multiple observations: over illumination, the low-volatility nitrogen mass increased from 0.055 to $0.062 \mu\text{g m}^{-3}$; the N/C ratio of DOM_{OA} increased from 0.045 to 0.054; and the AMS $\text{NO}_2^+/\text{NO}^+$ ratio decreased from 1.37 to 0.72, a shift commonly interpreted as increased contribution of organic nitrates (Day et al., 2022; Farmer et al., 2010). The sustained increase in Factor 3 suggests that aqueous-phase photochemistry leads to the formation of a highly functionalized, low-volatility organic fraction that may be a significant contributor to SOA-like material in ambient fog or cloud water.

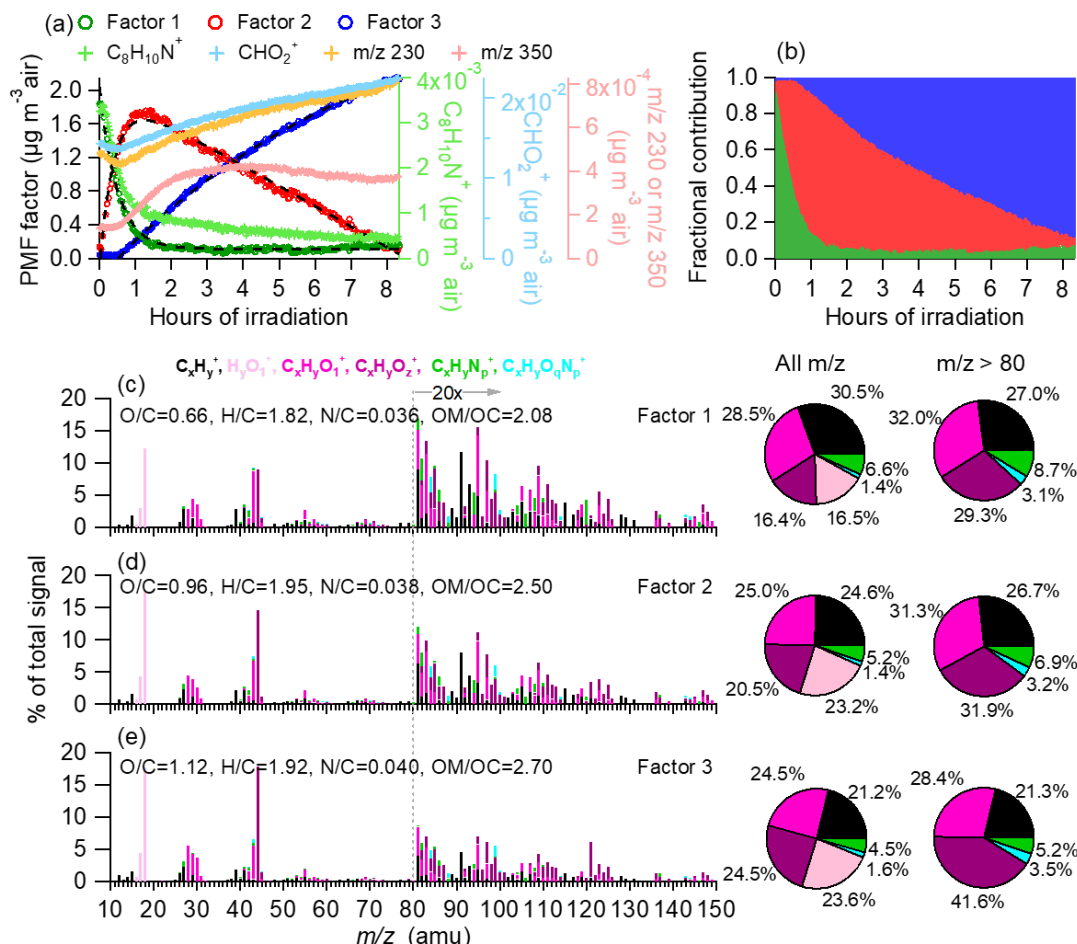
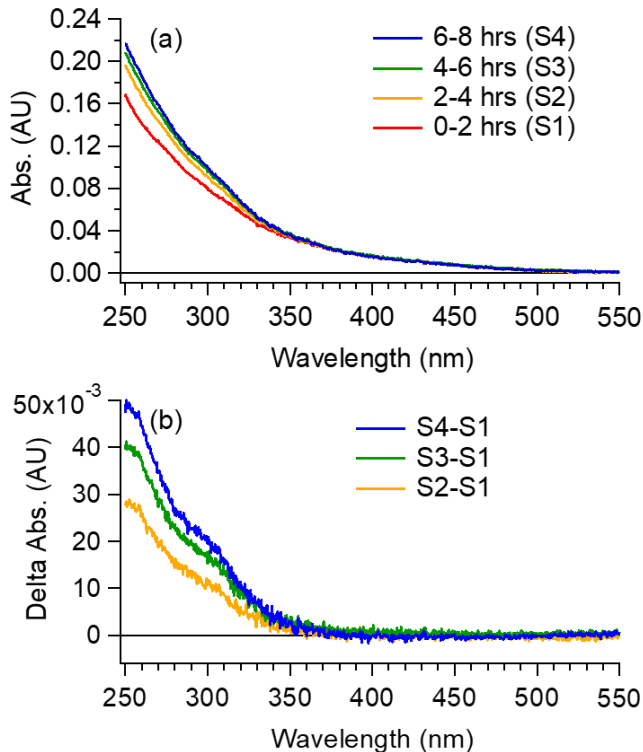


Figure 5. (a) Time series of the three-factor PMF solutions as well as tracer ions (e.g., $\text{C}_8\text{H}_{10}\text{N}^+$, CHO_2^+ , m/z 230, and m/z 350) representative of the three PMF factors. Factor 1 is fitted with a three-parameter single exponential function: $\text{DOM}_{\text{OA-Fac1}} = 0.11 + 1.9e^{-2.0t}$. Factor 2 is fitted with a five-parameter double exponential function: $\text{DOM}_{\text{OA-Fac2}} = 15.6 - 2.1e^{-2.6t} - 13.6e^{0.016t}$. Factor 3 is fitted with a three-parameter single exponential function: $\text{DOM}_{\text{OA-Fac3}} = 3.3 - 3.6e^{-0.13t}$. (b) Fractional contributions of the three PMF factors over time. (c-e) HR-AMS spectra of Factor 1, Factor 2, and Factor 3, respectively, with ion signals color-coded by six categories: C_xH_y^+ ,

320 H_3O_1^+ , $\text{C}_x\text{H}_y\text{O}_1^+$, $\text{C}_x\text{H}_y\text{O}_2^+$, $\text{C}_x\text{H}_y\text{N}_p^+$, and $\text{C}_x\text{H}_y\text{O}_q\text{N}_p^+$. Ion signals at $m/z \geq 80$ are enhanced by a factor of 20 for clarity. Calculated atomic ratios are shown in the legends. The pie charts show the relative contributions of different ion categories to each factor.

3.4 Photoinduced changes in light absorption and volatility of fog DOM

325 The optical properties of DOM in atmospheric waters have received increasing attention due to their contribution to brown carbon and their influence on Earth's radiative balance through solar absorption (Shapiro et al., 2009). To examine how fog water DOM evolves under photochemical processing, we measured its UV-visible absorbance at defined time intervals throughout the experiment. As shown in Fig. 6a, the initial fog water DOM exhibited strong absorbance in both the UV and visible regions, particularly between 300 and 500 nm relevant to tropospheric solar radiation. This absorption is attributed to conjugated chromophores, including HMW aromatic and polymeric compounds.



330 **Figure 6. Evolution of UV-visible absorption of fog water sample during simulated sunlight exposure. (a) UV-visible absorbance spectra of fog water samples collected at successive illumination intervals: S1 (0–2 h), S2 (2–4 h), S3 (4–6 h) and S4 (6–8 h). (b) Differential absorbance spectra of samples S2–S4 relative to the initial sample S1.**

335 Despite substantial chemical transformation of the DOM (e.g., increased oxidation, nitrogen incorporation, molecular fragmentation, and polymerization), the overall UV-vis spectrum revealed only modest changes over the 8-hour irradiation period. Differential absorbance spectra (relative to the initial sample, S1; Fig. 6b) revealed a slight increase in the 280–350 nm range, suggesting the formation of new light-absorbing chromophores during photochemical aging. These results indicate that aqueous-phase oxidation can sustain, and in some cases regenerate, the light-absorbing functionality of fog water DOM. This is consistent with AMS and ESI-MS observations of CHON species formation, which likely include chromophores such as

nitroaromatics and imidazoles. Although photobleaching of brown carbon chromophores is frequently assumed and has been widely observed during atmospheric aging (Hems and Abbatt, 2018; Laskin et al., 2015; Leresche et al., 2021), both laboratory and field studies have shown that aging can also enhance light absorption through the formation of new chromophores (Bianco et al., 2020; Hems et al., 2021; Laskin et al., 2025; Wu et al., 2024). Consistent with these observations, our experiments indicate that brown carbon-like optical properties can persist or even intensify during aqueous-phase processing. In particular, we observed evidence of oligomer formation, which likely contributes to the generation of new light-absorbing species. These processes have important implications for the radiative forcing potential of aged OA.

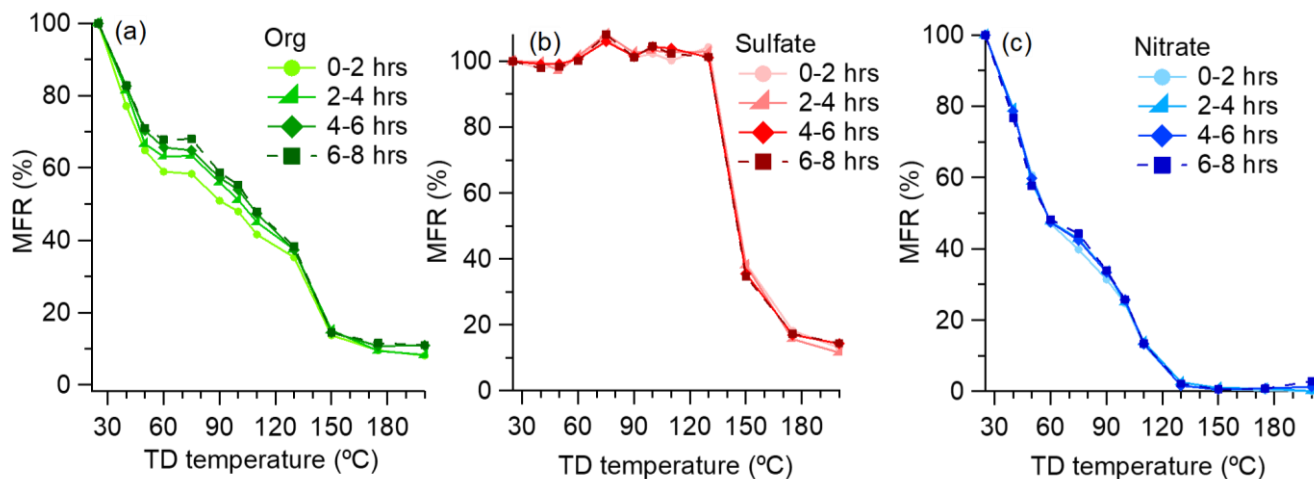


Figure 7. Mass fraction remaining (MFR, %) of (a) organics, (b) sulfate, and (c) nitrate in fog water-derived aerosols as a function of thermodenuder temperature. Each panel displays MFR trends across four irradiation periods (0-2, 2-4, 4-6, and 6-8 hours of simulated sunlight illumination).

To measure volatilities of fog-derived aerosols, we analyzed samples using HR-AMS downstream of a digitally controlled thermodenuder (TD (Fierz et al., 2007)), which included a bypass line and a heated line ending in an activated carbon cloth section. The TD cycled through seven set temperatures (25, 40, 65, 85, 100, 150, and 200 °C) hourly, with an automated three-way valve switching between bypass and heated modes every 5 minutes. Comparing AMS signals between these modes allowed us to assess the volatility profiles of fog water-derived aerosols. Figure 7 shows the mass fraction remaining (MFR) of organic materials (DOM_{OA}), sulfate, and nitrate as a function of thermodenuder temperature over different irradiation periods. While sulfate (Fig. 7b) and nitrate (Fig. 7c) displayed consistent volatility profiles throughout the experiment, DOM_{OA} (Fig. 7a) exhibited a clear evolution over time. Specifically, the MFR curves became progressively less steep with increased irradiation, indicating the net formation of less volatile organic species. This trend is consistent with our chemical analyses results, which show increased formation of multifunctional products and oligomers. The accumulation of highly functionalized, low-volatility compounds through aqueous-phase photochemical reactions may significantly impact the atmospheric lifetime and climate-relevant properties of OA.

4. Conclusions and atmospheric implications

This study examined the photochemical transformation of low-volatility DOM in fog water under simulated sunlight, equivalent to ~ 56 hours of wintertime tropospheric aging. The mass concentration of fog-derived DOM_{OA} increased steadily during illumination, largely due to functionalization reactions that incorporated O- and N-containing groups. Despite evidence of molecular fragmentation, total carbon mass remained largely stable, suggesting limited formation of volatile organics during aqueous-phase aging.

Both HR-AMS and positive-mode ESI-MS revealed increases in N-containing species following irradiation, along with the photooxidative transformation of CHN compounds into more oxygenated CHON and CHONS species. PMF analysis of the HR-AMS spectra resolved three distinct aging stages: unprocessed DOM_{OA} (Factor 1; O/C = 0.66, H/C = 1.82, N/C = 0.036), more oxidized intermediates (Factor 2; O/C = 0.96, H/C = 1.95, N/C = 0.038), and highly oxidized products (Factor 3; O/C = 1.12, H/C = 1.92, N/C = 0.040), with increasing O/C and N/C ratios across the factors. The accumulation of Factor 3 highlights fog processing as a source of O- and N-rich OA, potentially influencing aerosol hygroscopicity, light absorption, and toxicity. Supporting UV-vis and thermodenuder measurements confirmed that DOM_{OA} became increasingly more light-absorbing and less volatile with irradiation, consistent with the formation of highly functionalized, low-volatility species. Our findings are consistent with recent field observations in the Po Valley, Italy (Mattsson et al., 2025), which reported ON enhancement in fog water and fog residuals and attributed it to aqueous-phase formation of imidazoles. Although the Po Valley site is rural and our Fresno site is urban, both represent winter basin environments characterized by abundant liquid water and elevated nitrogen levels that favor aqueous processing and promote ON formation. The agreement between the Po Valley field observations and our laboratory aging experiments of Fresno fog DOM indicates that aqueous ON chemistry in fog is a broadly relevant pathway that may operate in diverse regions, with its magnitude influenced by local meteorology and emission sources. Overall, these results demonstrate that fog droplets act as chemically active microreactors, transforming dissolved organic matter into more oxidized, more light-absorbing and less volatile OA species during photochemical aging, beyond simply serving as scavengers of atmospheric pollutants (Collett et al., 2001, 2008; Kuang et al., 2020). Extensive laboratory and field studies have shown that oligomerization, acid formation, and imidazole formation proceed efficiently in the aqueous phase, producing aqSOA and brown carbon chromophores that can modify aerosol composition, light absorption, and hygroscopicity (Faust et al., 2017; Herrmann et al., 2015; Kuang et al., 2020; McNeill, 2015). Our results are consistent with prior findings and provide additional evidence for the influence of fog-driven aqueous processing on OA composition, ON speciation, volatility and light absorption. Given the frequent occurrence of winter fog and biomass burning in regions like California's San Joaquin Valley, fog-driven aqueous-phase processing likely plays a key role in regulating the atmospheric fate and climate-relevant properties of organic carbon and nitrogen. Although this study focuses on fog chemistry, similar processes are likely to occur in cloud water, with important implications for aerosol-cloud interactions and the oxidative evolution of atmospheric organic matter.

Code/Data Availability

All data and code used in the study are available from the corresponding author upon request.

395 Author contribution

LY, HK and YS collected fog samples and conducted experiments. WJ, LL, and LY analyzed the data. WJ, LY, and QZ wrote the manuscripts with input from all authors. QZ guided the research, managed the project, and defined the overarching strategy.

Competing interests

The authors declare that they have no conflict of interest.

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