Response to reviewers' comments on "**Photochemical Processing of Dissolved Organic Matter in Fog Water: Oxidation and Functionalization Pathways Driving Organic Aerosol Evolution**"

We thank the reviewer for their thoughtful and constructive comments, and we have revised the manuscript accordingly. Listed below are our point-to-point responses (in **black**) to the comments (in **blue**) and the changes made to the manuscript (in **red**).

Responses to Reviewer 1:

Comments:

This article presents a complete study of the evolution of DOM under irradiation using different techniques: aerosol mass spectrometry, ESI-Orbitrap, UV-vis absorption and volatility measurements. The manuscript is globally well written and the study is interesting and up to date. Nevertheless I have some concerns that need to be addressed before publication.

1. The sample was collected 15 years ago! How do you prove that DOM is not degraded at -20°C? For instance, standard solutions with micro and nanomolar concentrations of certain amino acids or carboxylic acids are not stable in the freezer for 2 years. I suppose that DOM composition was already changed compared to the composition in 2010. This hypothesis is supported by the fact that no short chain carboxylic acids or aldehydes are detected in this study (line 195).

Response: We would like to clarify that all experiments reported in this manuscript were performed in February 2015, about 5 years after collection of the fog samples. The composite used for the photochemical experiments consisted of three consecutive fog samples. Although multiyear storage (in the dark at - 20 °C) can potentially affect certain labile compounds, these samples were also analyzed shortly after collection in 2010, and the results were reported by Kim et al. (2019). The HR-AMS spectrum of the unilluminated fog sample in the present study is highly consistent with that reported by Kim et al. (2019), indicating that the DOM composition remained largely unchanged during storage. Additionally, Kim et al. (2019) confirmed the absence of dissolved VOCs in these fog samples, minimizing concerns about loss of volatile components that could bias our results. We have clarified this in the Experimental Method as follows:

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 study is highly similar to the spectra reported by Kim et al. (2019), indicating that DOM_{OA} composition remained largely unchanged during storage.

2. The authors froze the sample before irradiation: have you measured H2O2 before and after freezing? H2O2 is not stable in frozen samples and maybe what you observed is just direct photolysis, which would explain the predominant oligomerization on fragmentation. Please, state on this consideration in the manuscript, and maybe plan a future experiment where you have both direct photolysis and OH mediated.

Response: We did not measure H_2O_2 in the samples. However, H_2O_2 and multiple aqueous oxidants (e.g., •OH, $^3C^*$, and $^1O_2^*$) can be produced during illumination in the photochemical experiments. $^3C^*$ can form when brown carbon chromophores in fog water absorb light and undergo intersystem crossing (McNeill and Canonica, 2016). Energy transfer between $^3C^*$ and dissolved O_2 yields $^1O_2^*$ (Kaur and Anastasio, 2017; Ossola et al., 2021). H_2O_2 can be generated via energy/electron transfer of $^3C^*$ (Anastasio et al., 1997), which can subsequently undergo photolysis to produce •OH. Additionally, •OH can be generated from nitrate and nitrite photolysis in fog water (Brezonik and Fulkerson-Brekken, 1998). Therefore, even if pre-existing H_2O_2 degraded during storage, multiple oxidants are involved in our experiments, and the photochemistry is not limited to direct photolysis. We have clarified this in Section 2.2 as follows:

Under this condition, a variety of oxidants, such as hydroxyl radical (•OH), nitrate radical (•NO_3), triplet states of organic carbon ($^3C^*$), and singlet molecular oxygen ($^1O_2^*$), can be produced during illumination and react with dissolved organics in the aqueous phase. $^3C^*$ can form when brown carbon chromophores in fog water absorb light and undergo intersystem crossing (McNeill and Canonica, 2016). Energy transfer between $^3C^*$ and dissolved O_2 yields $^1O_2^*$ (Kaur and Anastasio, 2017; Ossola et al., 2021). H_2O_2 can be generated via energy/electron transfer of $^3C^*$ (Anastasio et al., 1997), which can subsequently undergo photolysis to produce •OH. Additionally, •OH can be generated from nitrate and nitrite photolysis in fog water (Brezonik and Fulkerson-Brekken, 1998).

3. I perfectly understand the difficulty of sampling enough fog (in volume) to conduct the experiment, but I still think that drawing general conclusions with the analysis of only one sample is risky. Especially considering that the sample was frozen for 15 years.

Response: The fog water sample used in this study was a composite of three back-to-back samples collected on Jan 9, 2010, and our experiments were conducted in February 2015. There was minimal change in the sample composition during storage, and we have clarified this in response to Comment 1.

In addition, the chemical composition of the fog samples used in this study is highly similar to that of other winter fog water samples collected in Fresno (Kim et al., 2019) and exhibits similar HR-AMS spectral features to winter fog samples collected in Davis, CA (unpublished results). Together, these observations suggest that the composite sample used in this study is representative of winter fogs in California’s Central Valley. We have clarified this point in the Experimental Method:

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.

4. Do you have information about the pH of the sample, its ionic composition, and the total DOC?

Response: Yes, the pH, major inorganic ions (measured by ion chromatography), and total DOC (measured by a TOC analyzer) of the three fog samples composited for our photochemical experiments have been reported in Kim et al. (2019). The fog water was near-neutral (pH 6.98-7.37) and nitrate-rich, representative of typical winter Fresno fogs. The DOM concentration was ~13.42 mgC L^{-1} (corresponding to 23.08 mg L^{-1} and 2.16 μg m^{-3} organics in the air calculated using liquid water content = 93.6 mg m^{-3} and HR-AMS measured OM/OC = 1.72). To make these fog sample characteristics readily accessible, we have added Table S1 to the Supplement:

Table S1. Chemical composition of the three fog samples combined for photochemical experiments in this study

Three fog samples collected on 1/9/2010 1:30 - 8:30		
Average Concentration (mg L^{-1})[a]		pH[a]
Sulfate	9.51	
Ammonium	23.4	
Nitrate	40.49	6.98 - 7.37
Chloride	0.75	
Organics	23.08[b]	

a. Values are derived from Kim et al. (2019)

b. Calculated from DOC concentration (13.42 mgC L^{-1}) and HR-AMS measured OM/OC (≈1.72)

5. The spectrum of the lamps reported in Jing et al. 2021 shows emission at 280 nm, which is in the UVB-UVC region and in contrast with the statement line 65. Nevertheless, the reactor is a Pyrex one, which should stop wavelength below 300 nm. Please, clarify this point and specify if other filters were used. Could you also clarify if the optical depth of the irradiated solution decreased during irradiation? I actually don't think so, but I prefer to have no doubt about it.

Response: We thank the reviewer for this comment; we have clarified the illumination spectrum in Section 2.2:

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.

The optical depth of the solution did not decrease during illumination. As shown in Figure 6 of the manuscript, UV-vis absorbance slightly increased between 250–350 nm during illumination, suggesting increased optical depth and formation of chromophores.

6. I'm quite surprised that the authors analysed the samples in ESI +, while almost all the works cited about HR-MS of atmospheric aqueous samples used ESI – (except Altieri for CHNO-CHN). Could you please justify this choice?

Response: Winter fogs in Fresno are nitrogen-rich and the fog DOM is characterized by high N/C ratio and elevated concentrations of N-containing organics, such as amines, amino acids and imidazoles (Kim et al., 2019). Positive-mode ESI is particularly sensitive to these protonatable species. Given our interest in organic nitrogen chemistry, we therefore analyzed the samples in positive mode.

We have added the following text to Section 2.5:

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.

7. Paragraph 3.2 is just ESI-Orbitrap? Because it seems to be a mixture of Orbitrap and AMS results.

Response: Right, Section 3.2 integrates ESI-Orbitrap MS and HR-AMS data. We stated this at the beginning of Section 3.2:

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.

8. The figures presented in the article are particularly complex and merge a lot of information, especially Figs 1, 2 and 3. Is there a way to simplify the graphical representation of the information?

Response: We appreciate the reviewer's concern regarding figure complexity. To improve clarity, we have simplified Figure 2 by removing Panel 2e and moving Panels 2f and 2g to Figures S14 and S11 in the Supplement.

We retain Figures 1 and 3 in their current form. Figure 1 presents the AMS spectra, the fractional contributions of inorganic and organic species, and the ion family fractions for DOM_{OA} before and after illumination. Displaying these panels side by side allows readers to compare spectral changes with shifts in chemical composition. Figure 3 presents the ESI-MS difference spectrum between early and late illumination, along with histograms that quantify shifts in compound distributions. These histograms are essential for visualizing how DOM_{OA} compound population redistribute during aging. We believe the current organization of Figures 1 and 3 provides clear and the most informative representation of the data.

9. Line 178: what are HxO1+?

Response: We interpret "$H_xO_1^+$" in the comment as the HR-AMS ion family $H_yO_1^+$.

$H_yO_1^+$ denotes AMS ions containing hydrogen and one oxygen (primarily HO^+ and H_2O^+), as noted in the Figure 1 caption and on Lines 178-179. These ions can be generated during vaporization and ionization of ammonium sulfate and oxygenated organics (e.g., carboxylic acids and alcohols) (Aiken et al., 2007; Allan et al., 2004; Canagaratna et al., 2015). In the organic spectrum presented in the manuscript, the sulfate-derived $H_yO_1^+$ contributions have been subtracted, as described in Section 2.3.1, and the $H_yO_1^+$ shown are organic-derived.

We have added the following text to Section 3.1:

In HR-AMS, organic-derived $H_yO_1^+$ ions are generated during vaporization and ionization of oxygenated organics such as carboxylic acids and alcohols (Canagaratna et al., 2015). In Fig. 1f, $H_yO_1^+$ ions showed a slope of 1.39, suggesting formation of oxygenated organics.

10. Discussion lines 178-185: is the intensity of the signal kept into account for the discussion?

Response: On Lines 178-185 and in Figures 1e-j, we show fractional contributions of ions, instead of absolute intensities, when discussing changes in chemical composition. The purpose is to isolate chemistry from variations in DOM_{OA} mass. In contrast, when we discuss DOM_{OA} mass growth, we reply on absolute concentration and signal intensities.

To address this comment, we have added the scatter plots comparing the absolute signals of the AMS ions in Figure S10 for reference.

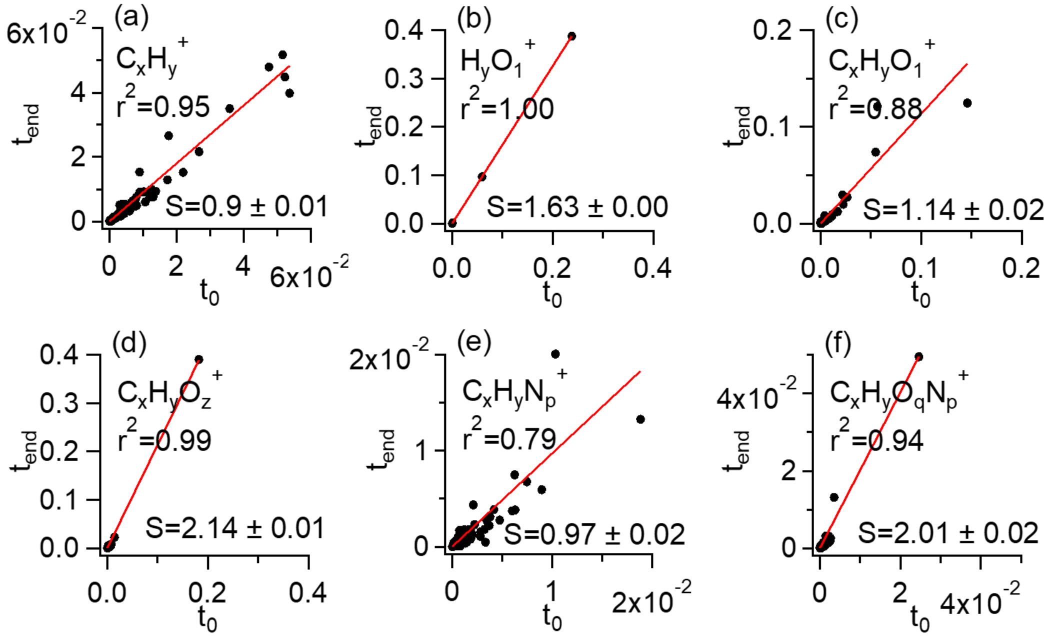

Figure S10. Comparison of the absolute signal intensities of organic AMS ion categories (i.e., $C_xH_y^+$, $H_yO_1^+$, $C_xH_yO_1^+$, $C_xH_yO_z^+$, $C_xH_yN_p^+$, and $C_xH_yO_qN_p^+$ ($x \geq 1$; $y \geq 1$; $z > 1$; $p \geq 1$; $q \geq 1$)) at t_0 and t_{end}. Red lines show orthogonal distance regression (ODR) fits; slopes (S) and correlation coefficients (r^2) are provided in each panel.

11. Line 182: "Lightly… molecules" I'm probably tired, but I really don't understand the sentence, especially "variability among individual ions indicates". Could you please rephrase?

Response: We have rephrased this sentence in the manuscript for clarification:

The overall fractional contribution of the lightly oxygenated ion family ($C_xH_yO_1^+$) 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.

12. Line 270: is the variation of N/C from 0.036 to 0.038 significant? Since I don't think so, the authors should not conclude about the incorporation of nitrogen compounds into DOM.

Response: We agree that the N/C increase from 0.036 to 0.038 is small and, on its own, not statistically persuasive evidence for nitrogen incorporation from Factor 1 to Factor 2. However, nitrogen incorporation during aging is supported by multiple observations. The low-volatility nitrogen mass increased from 0.055 to 0.062 µg m^{-3}, and the N/C of DOM_{OA} increased from 0.045 to 0.054 over 8 hours of illumination. In addition, the AMS NO_2^+/NO^+ ratio decreased from 1.37 to 0.72, a shift commonly interpreted as increased contribution of organic nitrates relative to inorganic nitrate (Day et al., 2022; Farmer et al., 2010). These observations all indicate incorporation of nitrogen into DOM_{OA}.

For clarification, we have modified the text in Section 3.3 as follows:

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 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 μg m^{-3}; the N/C ratio of DOM_{OA} increased from 0.045 to 0.054; and the AMS NO_2^+/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).

13. Line 307: "in contrast with the assumption of photobleaching" please add a reference to this assumption. Other papers suggest the formation of brown carbon instead of photobleaching (Bianco et al. Tryptophan, 2016; Paglione et al, 2014)

Response: We agree that both photobleaching and browning can occur during photochemical aging of fog DOM. Pre-existing chromophores can undergo fragmentation and ring-opening reactions to yield smaller, highly oxidized products, which reduce light absorption (Hems and Abbatt, 2018; Laskin et al., 2015; Leresche et al., 2021). On the other hand, new chromophores, such as oligomers, quinones, nitroaromatics, and N-heterocycles with high conjugation, can form, leading to browning (Bianco et al., 2020; Hems et al., 2021; Laskin et al., 2025; Wu et al., 2024).

We have added relevant citations and revised the text as follows:

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.

14. Conclusions: please, in the last few lines, remember that the study is performed on one sample collected more than 10 years ago. This article is good and well written, but more evidence is needed to confirm that fog-driven aqueous phase processes regulate the climate-relevant properties of organic carbon and nitrogen.

Response: As noted earlier, the fog sample we used in this study was a composite of three consecutive fog samples representative of winter fogs in California's San Joaquin Valley. The sample composition remained largely unchanged during storage between collection and the

February 2015 experiments, as evidenced by the close agreement between the HR-AMS spectrum of the unilluminated sample in this study and that measured shortly after collection (Kim et al., 2019). Accordingly, we are confident that the observed chemical evolution, including oxidation of ON species, fragmentation, functionalization, oligomerization, organic acid formation, and chromophore formation, accurately reflects photochemical aging processes in fog DOM.

The key role of aqueous-phase processing has been well-established by extensive lab and field studies (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.

We have added the following sentence to the conclusion:

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.

Responses to Reviewer 2:

The study by Jiang et al. presents very interesting results on photochemical aging of dissolved organic matter (DOM) in fog water. The concept of the experiments is to illuminate fog samples while continuosly atomize the solutions and analyze the particles using a HR-ToF-AMS. This a very interesting concept because it allows to study the photochemical processing in real time. The scope of the study fits well to ACP, so that it should be published. However, the consequences of the long time between sampling the fog water and the analysis should be discussed (see major comment below).

Major comments:

I agree with referee #1 that the main problem is the age of the samples. Actually, the data of the laboratory analysis is not given, but it is to assume that this was only done recently.

Maybe it is not possible now to prove that the samples have not aged during the many years of storage, but this issue should be discussed. Are there no newer, more recent samples that can be/were studies with the same technique? If they show the same result, it will be an important indication that the presented data of the 2010 samples are valid.

Response: We would like to clarify that all experiments reported in this manuscript were performed in February 2015, about 5 years after collection of the fog samples. The composite used for the photochemical experiments consisted of three consecutive fog samples. Although multiyear storage (in the dark at - 20 °C) can potentially affect certain labile compounds, these samples were also analyzed shortly after collection in 2010, and the results were reported by Kim et al. (2019). The HR-AMS spectrum of the unilluminated fog sample in the present study is highly consistent with that reported by Kim et al. (2019), indicating that the DOM composition remained largely unchanged during storage. In addition, the chemical composition of the fog samples used in this study is highly similar to that of other winter fog water samples collected in Fresno (Kim et al., 2019) and exhibits similar HR-AMS spectral features to winter fog samples collected in Davis, CA (unpublished results). Together, these observations suggest that the composite sample used in this study is representative of winter fogs in California's Central Valley.

We have clarified this in the Experimental Method as follows:

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 study is highly similar to the spectra reported by Kim et al. (2019), indicating that $\mathrm{DOM_{OA}}$ 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.

Minor comments:

- lines 174-176: You mention the formation of organic nitrate:

There is the AMS metric of NO2+/NO+ to obtain information on organic nitrates as opposed to inorganic nitrates (e.g. Day et al., AMT 2022): Did you look at this? Did the ratio NO2/NO change over time?

Response: Thank you for the suggestion. Figure S9 has been added to show the NO_2^+/NO^+ ratio change during fog water photochemical aging. The NO_2^+/NO^+ ratio decreased from 1.37 to 0.72 over illumination, indicating an increase in organic nitrate contribution. However, since we did not perform pure NH4NO3 measurements during the experiment, we are not able to calculate the contribution of particle organic nitrate quantitatively.

We have added the following materials to the manuscript:

The AMS NO_2^+/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).

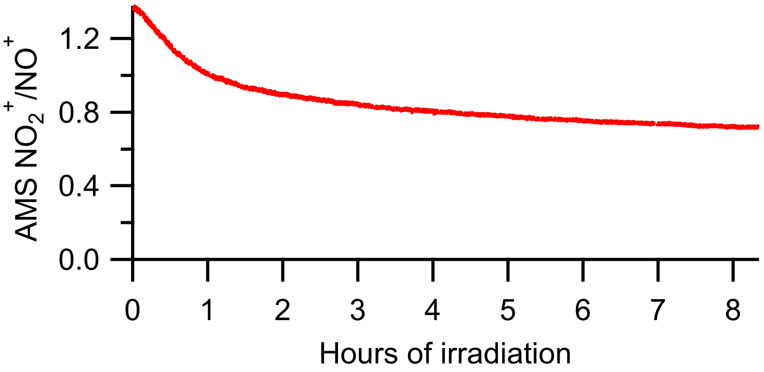

Figure S9. AMS NO_2^+/NO^+ ratio of the fog sample during photochemical aging

- Figure 2: Please explain f_43, f_44, etc. for the non-AMS experts. Especially the difference between f_44 and f_CO2 etc. Adjust caption for d) (f_44 vs f_43, f_CO2 vs f_C2H3O+). Same for e). Is f_60 the same as f_C2H4O2+? Most likely not, because f_60 is UMR and f_C2H4O2+ is HR. Also, please add motivation of showing the "f60" plot. f60 is typically used a biomass burning marker. Explain the line labeld "0.003". In the caption and explanation of shaded region in Fig 2d, you should reference Ng et al., 2011. Are Figs 2d,e,g mentioned in the main text all? I think not. If that is so, why showing them?

Response: We have updated the Figure 2d caption to explain f_{43}, f_{44}, f_{CO2+}, f_{C2H3O+} and the shaded triangle region, citing Ng et al. (2010, 2011). We now cite Fig. 2d in Section 3.1:

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).

Fig. 2e (f_{CO2+} vs. $f_{C2H4O2+}$ plot) was originally included as a quick check for biomass-burning influence in fog water and potential aging of BBOA in fog DOM, given that residential wood burning is common in winter Fresno. However, since this plot is ancillary and the result shows low BB signatures (e.g., m/z 60 and $C_2H_4O_2^+$), we have removed this panel to avoid overloading the reader.

To reduce the complexity of Figure 2, Figures 2f and 2g have been moved to Figures 14 and 11 in the Supplement. Fig. 2g (now Fig. S11) shows a decrease in $C_xH_yN_z^+/C_xH_yO_zN_p^+$ ratio during illumination, indicating oxidation of organic-nitrogen species and formation of functionalized N-containing products. We now cite this figure in Section 3.3:

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.

Below is the revised Figure 2.

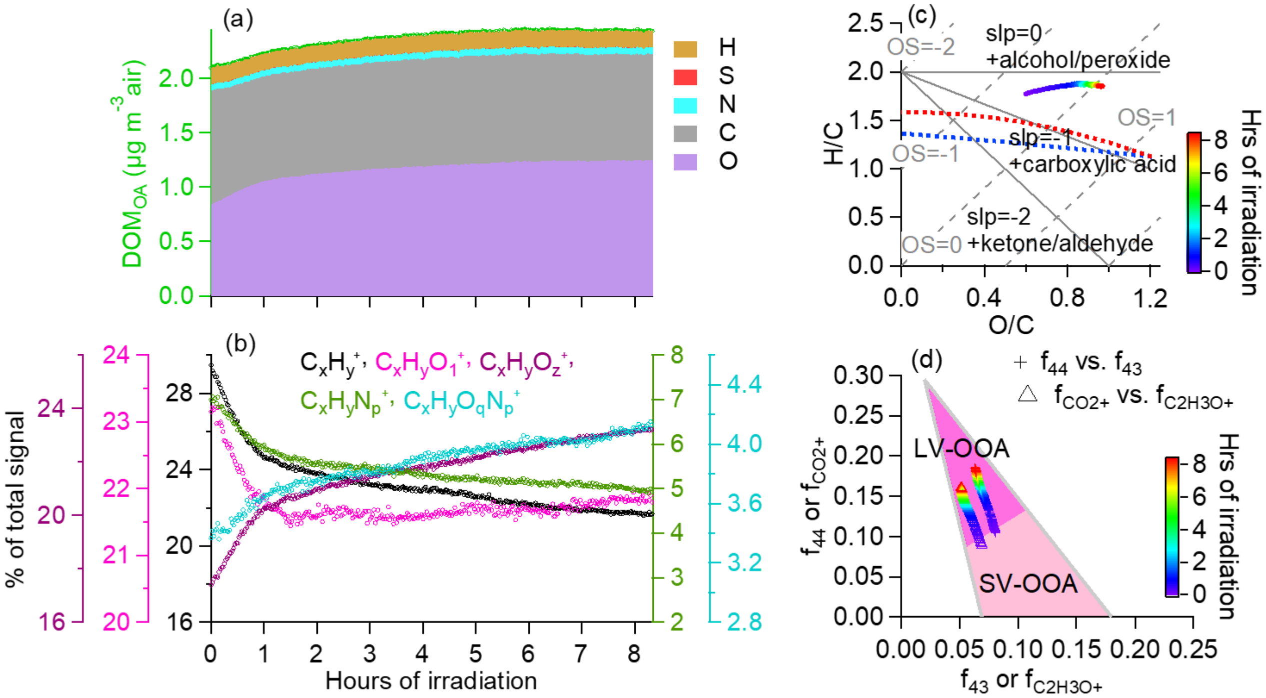

Figure 2. Time evolution of DOM_{OA} composition during simulated sunlight illumination. (a) DOMOA concentration and stacked mass contributions from O, C, N, S and H atoms. The mass concentrations represent ambient air concentrations, calculated by normalizing the liquid-phase concentrations to the sampled 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 $C_xH_yO_qN_p^+$ ($x \geq 1$; $y \geq 1$; $z > 1$; $p \geq 1$; $q \geq 1$). (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_{CO2+} (fraction of CO_2^+ ion) and f_{C2H3O+} (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).

- It might be interesting to show the fractional mass contribution of all main AMS compounds over time (in the supplement). Fig 1d shows it only for t_0 and t_end.

Response: We have added the time series of the fractional contributions of AMS-measured nitrate, sulfate, ammonium, chloride, and organics in Figure S7.

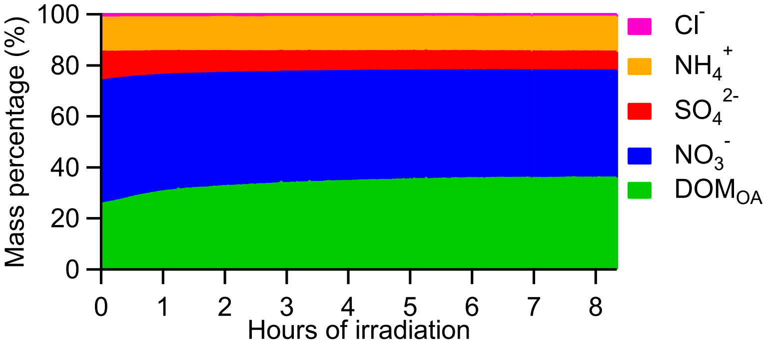

Figure S7. Mass fractions of major inorganic species and DOMOA during fog water photochemical aging

Technical remarks:

- Figure 1:

In Figure 1d the color legend is missing. Please state that it is the same as in a-c

In figure caption to (d): I suggest adding "ion categories": Mass fractions of major inorganic species and DOM_OA ion categories at t_0 and t_end.

Response: We have updated the legend and caption for Figure 1d according to your comments.

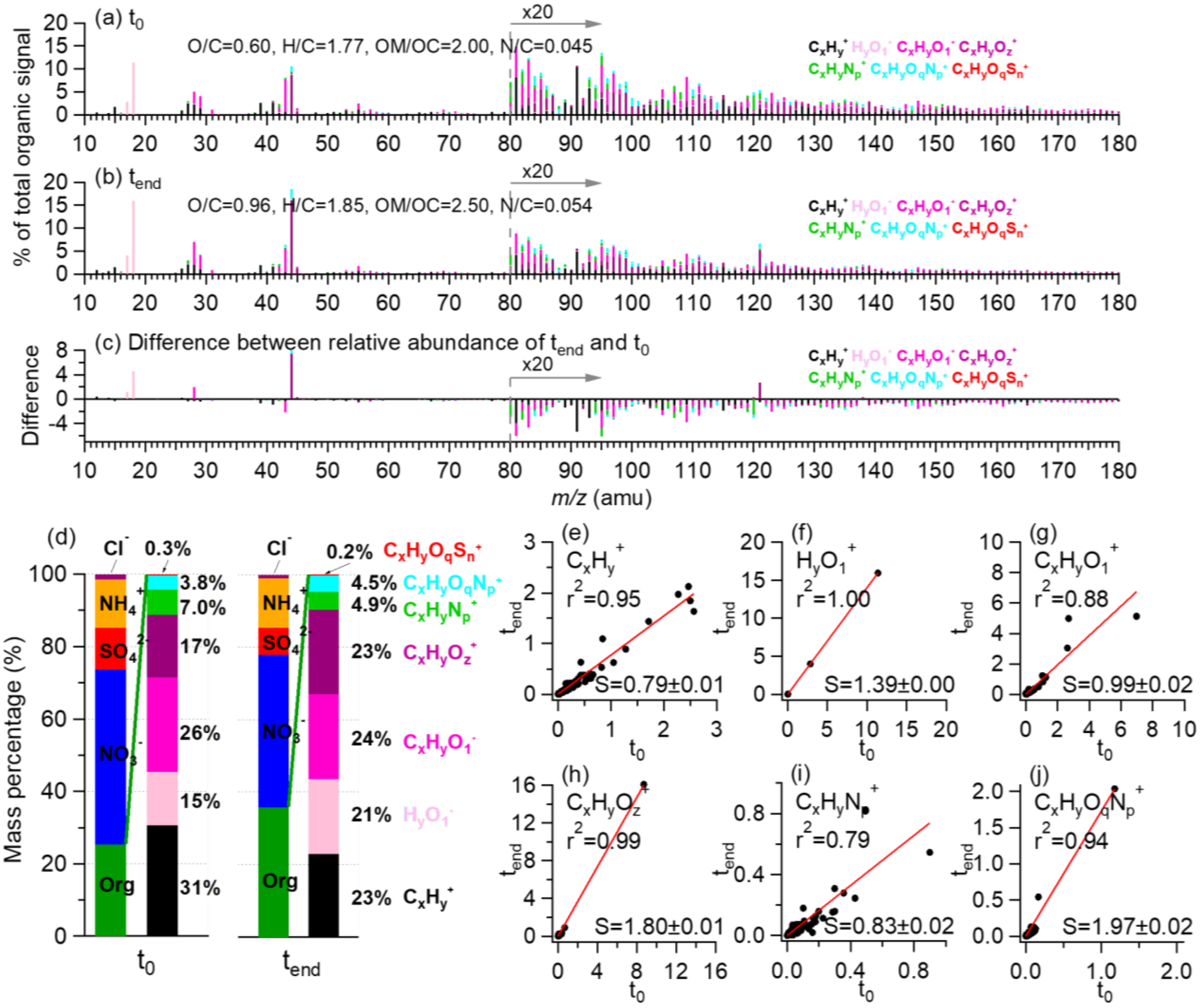

Figure 1. Overview of DOM_{OA} composition before (t_0) and after (t_{end}) eight hours of simulated sunlight illumination. (a-c) HR-AMS spectra of DOM_{OA} at t_0 and t_{end}, and the difference spectrum between them (t_{end} minus t_0), with peaks color-coded by ion categories: $C_xH_y^+$, $H_yO_1^+$, $C_xH_yO_1^+$, $C_xH_yO_z^+$, $C_xH_yN_p^+$, and $C_xH_yO_qN_p^+$ ($x \geq 1$; $y \geq 1$; $z > 1$; $p \geq 1$; $q \geq 1$). 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.

Responses to Reviewer 3:

Comments:

The authors studied how fog water containing DOM can generate indirect photochemical changes in organic matter. The authors use a nice suite of instruments and characterizations to show this photochemical oxidation process. For example, the authors show photo-functionalization through the addition of oxygen and nitrogen-containing groups. The PMF analysis is a good addition data analysis tool to showcase the progression of the aging. This manuscript can be considered for publication once the authors have considered the following points.

Experimental setup:

1. The authors should add the irradiance spectra (could be added in the SI) for the irradiation setup. Adding the sum of output spectra of the different bulbs at different wavelengths will help in the comparison with the solar spectrum.

Response: We have added Figure S1 to show the normalized photon flux spectrum inside the photoreactor. The RPR-200 illumination system has been previously characterized (George et al., 2015), which reported a ~7 times faster photochemistry relative to winter solstice midday sunlight in Northern California. We now cite this in Section 2.2 and modify the text as follows:

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.

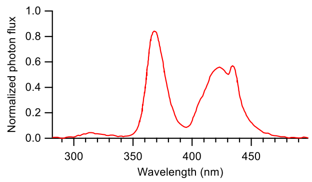

Figure S1. Normalized distribution of the photon fluxes inside the RPR-200 illumination system (George et al., 2015; Jiang et al., 2021)

2. The equivalence to "~56 hours of winter solstice sunlight" is mentioned but would have required actinometry and conversion factors. Could the authors report these experimental details and equations?

Response: The RPR-200 illumination system has been previously characterized (George et al., 2015), which reported a ~7 times faster photochemistry relative to winter solstice midday sunlight in Northern California. Based on this, we estimate that the ~8 h of illumination in our experiment is equivalent to ~56 h of winter solstice midday sunlight exposure. We now cite this in Section 2.2 and clarify as follows:

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.

Sample representativeness:

3. Only three fog samples from a single day (Jan 9, 2010) were pooled. These samples represent a very limited dataset for generalization. There could be aging occurring overtime that needs to be specifically addressed. Referring to "Resch et al, *Environ. Sci. Technol.* 2024, 58, 32, 14318–14328" could also be useful.

Response: The chemical composition of the three fog samples is highly similar to that of other winter fog water samples collected in Fresno (Kim et al., 2019) and exhibits similar HR-AMS spectral features to winter fog samples collected in Davis, CA (unpublished results). This suggests that the samples used in this study are representative of winter fogs in California's Central Valley.

Additionally, we would like to clarify that all experiments reported in this manuscript were performed in February 2015, about 5 years after collection of the fog samples. Although multiyear storage (in the dark at - 20 °C) can potentially affect certain labile compounds, these samples were also analyzed shortly after collection in 2010, and the results were reported by Kim et al. (2019). The HR-AMS spectrum of the unilluminated fog sample in the present study is highly consistent with that reported by Kim et al. (2019), indicating that the DOM composition remained largely unchanged during storage. We have clarified this in the Experimental Method as follows:

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 study is highly similar to the spectra reported by Kim et al.

(2019), indicating that $\mathrm{DOM_{OA}}$ 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.

4. The implications for variability (seasonal, meteorological, source-related) can be added in order to contextualize the results. Considering the body of research on fog samples from the Po Valley, Italy, I recommend that the authors extend their discussion to include references like Mattsson et al, ACP, 25, 7973–7989, 2025. Including more explicit connections to ambient implications, beyond Fresno, can strength the atmospheric relevance.

Response: Thank you for this suggestion. We now cite Mattsson et al. (2025), which reported ON enhancement in fog water and fog residuals in the Po Valley. The agreement between their field observations and our lab aging experiments allows us to place our findings in a broader ambient context. We have added the following text to the Conclusions and atmospheric implications:

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.

Definition of $\mathrm{DOM_{OA}}$:

5. The definition "low-volatility fraction of DOM that forms OA upon water evaporation" remains vague. The cutoff for volatility and how it was operationally determined should be better explained. Does it come from literature? If yes, could the authors add these references?

In this study, $\mathrm{DOM_{OA}}$ is an operational definition tied to our AMS workflow. The fog water was aerosolized and dried prior to AMS measurements. Compounds that completely volatilize during this step are not captured by AMS, while the low-volatility fraction that remains in the particle phase is detected by AMS and is defined as $\mathrm{DOM_{OA}}$. This nebulizer-dryer-AMS approach has been widely used in fog studies (Brege et al., 2018; Kim et al., 2019; Mattsson et al., 2025).

We have now clarified this in the Introduction and Section 2.2:

In the Introduction:

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.

In Section 2.2:

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).

Light absorption:

6. The literature reports photobleaching more often after irradiation. The authors instead report photo browning, so they should address this discrepancy with the literature and contextualize better the results. Why are the authors not seeing photobleaching? Because of the length of irradiation? Are there other studies of similar samples showing the same property?

Both photobleaching and browning can occur during photochemical aging of fog DOM. Pre-existing chromophores can undergo fragmentation and ring-opening reactions to yield smaller, highly oxidized products, which reduce light absorption (Hems and Abbatt, 2018; Laskin et al., 2015; Leresche et al., 2021). On the other hand, new chromophores, such as oligomers, quinones, nitroaromatics, and N-heterocycles with high conjugation, can form, leading to browning (Bianco et al., 2020; Hems et al., 2021; Laskin et al., 2025; Wu et al., 2024).

We have added relevant citations and revised the text as follows:

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.

Technical points

7. The authors should refer and describe all the figures (figure 2d, 2e, 2g are not mentioned in the text)

We now cite Fig. 2d in Section 3.1:

"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)."

Fig. 2e (f_{CO2+} vs. $f_{C2H4O2+}$ plot) was originally included as a quick check for biomass-burning influence in fog water and potential aging of BBOA in fog DOM, given that residential wood burning is common in winter Fresno. However, since this plot is ancillary and the result shows low BB signatures (e.g., m/z 60 and $C_2H_4O_2^+$), we have removed this panel to avoid overloading the reader.

To improve clarity, we have moved Fig. 2g to Fig. S11 in the Supplement. Fig. 2g (now Fig. S11) shows a decrease in $C_xH_yN_z^+/C_xH_yO_zN_p^+$ ratio during illumination, indicating oxidation of organic-nitrogen species and formation of functionalized N-containing products. We now cite this figure in Section 3.3:

"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."

8. The authors should label the species in the figures and in the text (for example line 207 and 210 page 8 and figure 2b shows different acronyms)

We have updated the ion category labels and acronyms to keep them consistent across the manuscript and figures. Figure 2 has been revised as follows:

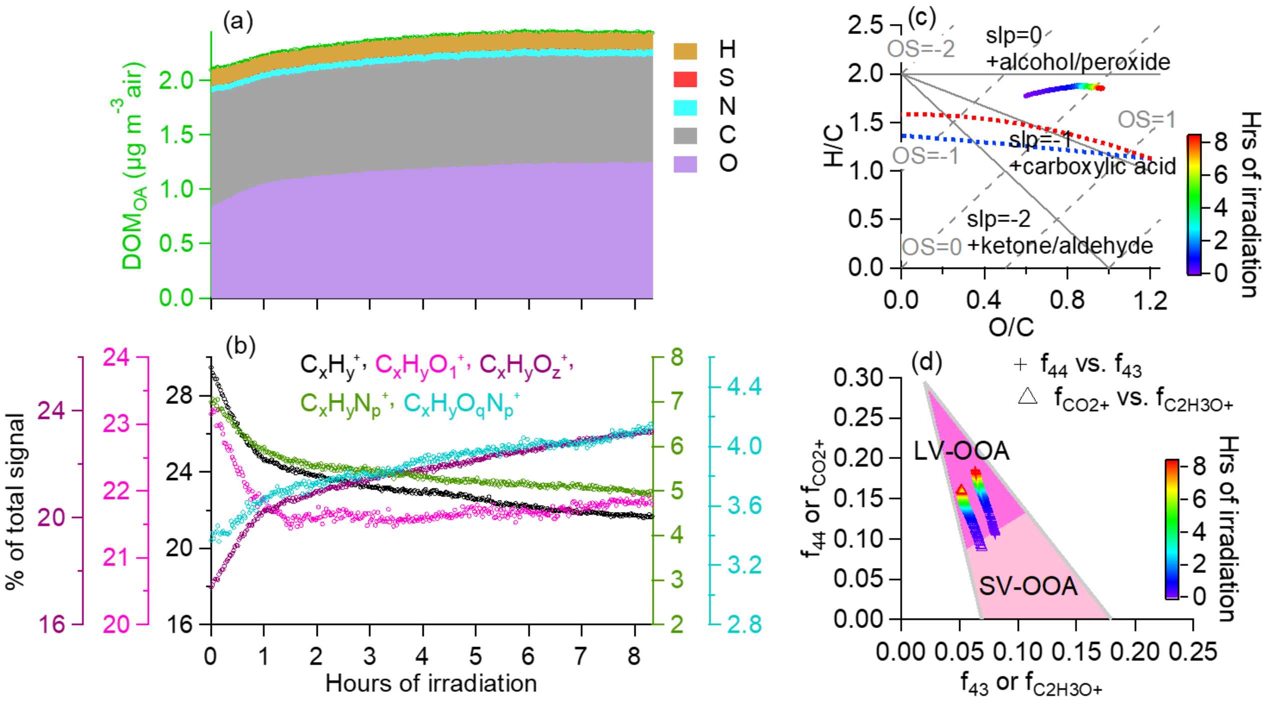

Figure 2. Time evolution of DOM_{OA} composition during simulated sunlight illumination. (a) DOMOA concentration and stacked mass contributions from O, C, N, S and H atoms. The mass concentrations represent ambient air concentrations, calculated by normalizing the liquid-phase concentrations to the sampled 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 $C_xH_yO_qN_p^+$ ($x \geq 1$; $y \geq 1$; $z > 1$; $p \geq 1$; $q \geq 1$). (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_{CO2+} (fraction of CO_2^+ ion) and f_{C2H3O+} (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).

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