Response to reviewer's 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	6.98 - 7.37
Ammonium	23.4	
Nitrate	40.49	
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 $\mathrm{DOM_{OA}}$ 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.

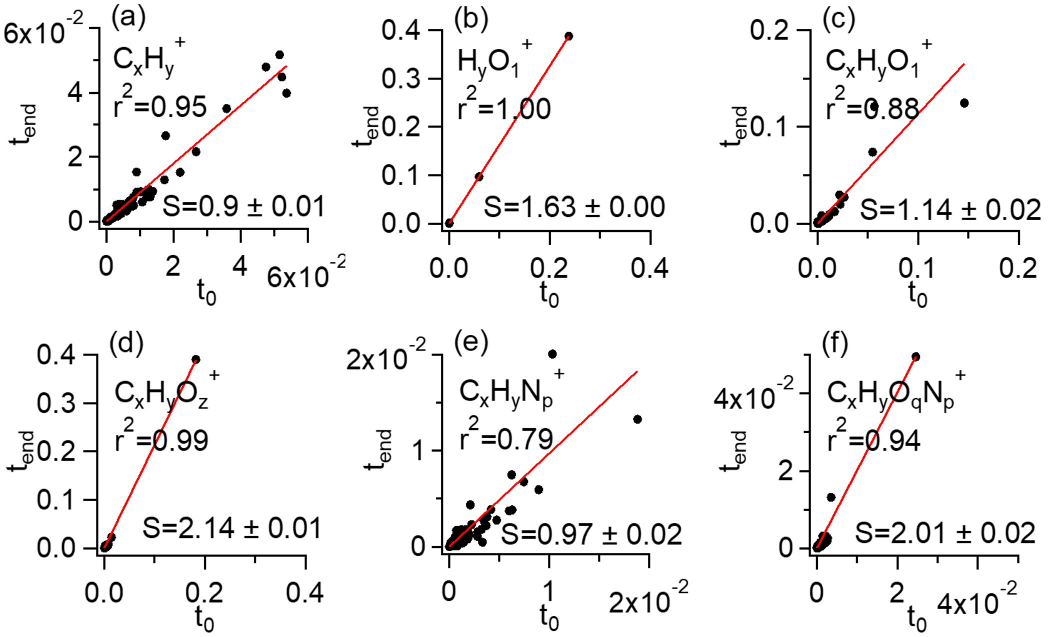

Figure S10. Comparison of the absolute signal intensities of organic AMS ion categories (i.e., $C_xH_y^+$, $H_yO_1^+$, $C_xH_yO_1^+$, $C_xH_yO_z^+$, $C_xH_yN_p^+$, and $C_xH_yO_qN_p^+$ ($x \geq 1$; $y \geq 1$; $z > 1$; $p \geq 1$; $q \geq 1$)) at t_0 and t_{end}. Red lines show orthogonal distance regression (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.

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