Referee #1

The introduction cites literature that has nothing to do with atmospheric aerosols and are based on photochemical studies of aquatic chromophoric dissolved organic matter. This is not stated here, and hence the references used here are inappropriate and misleading. Unfortunately the introduction did not improve and does not make correctly use of the primary literature. A lot of photochemical studies on aerosols are still missing and wrong citations have been used. Grammar remains distracting and some of the descriptions are confusing as a result of this. Overall, the manuscript improved slightly but remains poorly written and misused the literature. The overall novelty is still not clear to me, but perhaps the evaluation of the ROS is of merit. I am also concerned to combine optical data that were collected in different solvents because of the known substantial matrix effects associated with different solvent matrices. I still cannot recommend publication of this manuscript in its current state.

We appreciate the comments from reviewer. According to the reviewer's comments, we have revised this paper. The details are as follows. *The blue italics are comments of reviews. The red italics are improvements and original text of reviews.* The black font are responses.

We have improved the grammar and the descriptions. For example,

(1) We have corrected "*the physical and chemical characteristics of COM change significantly under sunlight exposure*" to "*the optical characteristics and components of COM change significantly under solar irradiation*" in improved paper.

(2) We have corrected "*Sunlight exposure cause the photo-bleaching of COM*" to "*optical properties change significantly due to chromophores are photo-bleached in aerosols*" in improved paper.

(3) We have corrected "*excited COM react with organic matter and generate secondary organic aerosols (Zhao et al., 2015; Saleh et al., 2013; Zhong and Jang, 2014; Lee et al., 2014; Liu et al., 2016)*" to "*For example, COM can be oxidized by hydroxyl radicals (•OH) (Zhao et al., 2015) and the formation of polyols can be attributed to photooxidation of isoprene, which could be initiated by •OH (Claeys et al., 2004)*" in improved paper.

(4) We have corrected "*As shown in the scatter plot (Fig.4), absorbance decreases significantly during photolysis. The decay kinetics of absorbance is different to fluorophores. The attenuation trend is inconstant, so the decay kinetics do not be mathematical analyzed and the absorbance also could confirm the photo-degradation of COM. As shown in Fig.4, the attenuation of fluorescence is mathematical analyzed and the number or shape of fluorophores do not change during COM photolysis*" to "*The attenuations of fluorescence and absorption coefficients are fit to first-order decay. The absorption coefficients decrease by 32.0% and TFV decreases by 71.4% on average. However, as shown in Fig.3, fluorescence intensities increase and decrease in different regions of EEMs (Aiona et al., 2018; Timko et al., 2015)*" in improved paper.

We also deleted the wrong citations. For example,

- ➢ *Cory, R. M., and McKnight, D. M.: Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter, Environ. Sci. Technol., 39, 8142-8149, http://dx.doi.org/10.1021/es0506962, 2005.*
- ➢ *Del Vecchio, R., and Blough, N. V.: Photobleaching of chromophoricdissolved organic matter in natural waters: kinetics and modeling, Mar. Chem., 78, 231–253, http://dx.doi.org/10.1016/S0304-4203(02)00036-1, 2002.*
- ➢ *Gonsior, M., Peake, B. M., Cooper, W. T., Podgorski, D., D'Andrilli, J., and Cooper, W. J.: Photochemically induced changes in dissolved organic matter identified by ultrahigh*

resolution fourier transform ion cyclotron resonance mass spectrometry, Environ. Sci. Technol., 43, 698-703, http://dx.doi.org/10.1021/es8022804, 2009.

- *Kieber, R. J., Adams, M. B., Wiley, J. D., Whitehead, R. F., Avery, G. B., Mullaugh, K. M., and Mead, R. N.: Short term temporal variability in the photochemically mediated alteration of chromophoric dissolved organic matter (CDOM) in rainwater, Atmos. Environ., 50, 112-119, http://dx.doi.org/10.1016/j.atmosenv.2011.12.054, 2012.*
- *Vodacek, A., Blough, N. V., DeGrandpre, M. D., Peltzer, E. T., and Nelson, R. K.: Seasonal Variation of CDOM and DOC in the Middle Atlantic Bight: Terrestrial Inputs and Photooxidation, Limnol. Oceanogr., 42, 231-253, http://dx.doi.org/10.1117/12.26643, 1997.*

We also added the citations about aerosol in improved manuscript. For example,

- *Budisulistiorini, S. H.; Riva, M.; Williams, M.; Chen, J.; Itoh, M.; Surratt, J. D.; Kuwata, M.: Light-Absorbing Brown Carbon Aerosol Constituents from Combustion of Indonesian Peat and Biomass. Environ. Sci. Technol., 51, 4415-4423, http://dx.doi.org/10.1021/acs.est.7b00397, 2017.*
- *Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; Jenkin, M. E.; Rossi, M. J.; Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II - gas phase reactions of organic species, Atmos. Chem. Phys., 6, 3625-4055, http://dx.doi.org/10.5194/acp-6-3625-2006, 2006.*
- *Carlton, A. G.; Turpin, B. J.; Altieri, K. E.; Seitzinger, S.; Reff, A.; Lim, H. J.; Ervens, B.: Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous photooxidation experiments, Atmos. Environ., 41, 7588-7602, http://dx.doi.org/10.1016/j.atmosenv.2007.05.035, 2007.*
- *Claeys, M.; Graham, B.; Vas, G.; Wang, W.; Vermeylen, R.; Pashynska, V.; Cafmeyer, J.; Guyon, P.; Andreae, M. O.; Artaxo, P.; Maenhaut, W.: Formation of secondary organic aerosols through photooxidation of isoprene, Science, 303, 1173-1176, http://dx.doi.org/10.1126/science.1092805, 2004.*
- *Mang, S. A.; Henricksen, D. K.; Bateman, A. P.; Andersen, M. P. S.; Blake, D. R.; Nizkorodov, S. A.: Contribution of Carbonyl Photochemistry to Aging of Atmospheric Secondary Organic Aerosol, J. Phys. Chem. A, 112, 8337-8344, http://dx.doi.org/10.1021/jp804376c, 2008.*

The novelty of the paper is (1) highlighting the effect COM photodegradation on carbonaceous components, optical properties, fluorophores in different aerosols; (2) illustrating changes in photochemical activity during COM photodegradation process by the method of probing triplet state and ROS generation; (3) exploring the mechanism of COM photodegradation affecting aerosol aging. In order to clear the overall novelty, we have revised the last paragraph in Sec 1. "*The objectives of the study are (1) to clarify the characteristics of carbonaceous components variation during COM photolysis, (2) to explore the effects of photo-degradation on the components and optical properties of water-soluble and water-insoluble chromophores, and (3) to investigate the effects of COM photo-degradation on photochemical reactivity and aerosol aging (photochemical reactivity is characterized by triplet state and singlet oxygen generation capacity)*".

Specific comments:

1. Line 10: HULIS needs to be defined.

According to the reviewer's suggestion, we have corrected "*there is a transformation from low oxidation to high oxidation HULIS and high oxidation HULIS*" to "*low oxidation humic-like substance (HULIS) is converted into high oxidation HULIS*" in improved paper.

2. Line 38: Murphey et al 2018 did not study aerosols. This study was undertaken with dissolved organic matter from different aquatic systems and cannot be directly compared to aerosols.

According to the reviewer's suggestion, we have deleted the wrong citations.

We have deleted "*Murphy et al. reported that fluorescence intensity of chromophores decreased after 20 h of simulated solar irradiation (Murphy et al., 2018)*".

We have deleted the citations about aquatic systems, for example,

- ➢ *Cory, R. M., and McKnight, D. M.: Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter, Environ. Sci. Technol., 39, 8142-8149, http://dx.doi.org/10.1021/es0506962, 2005.*
- ➢ *Del Vecchio, R., and Blough, N. V.: Photobleaching of chromophoricdissolved organic matter in natural waters: kinetics and modeling, Mar. Chem., 78, 231–253, http://dx.doi.org/10.1016/S0304-4203(02)00036-1, 2002.*
- ➢ *Gonsior, M., Peake, B. M., Cooper, W. T., Podgorski, D., D'Andrilli, J., and Cooper, W. J.: Photochemically induced changes in dissolved organic matter identified by ultrahigh resolution fourier transform ion cyclotron resonance mass spectrometry, Environ. Sci. Technol., 43, 698-703, http://dx.doi.org/10.1021/es8022804, 2009.*
- ➢ *Kieber, R. J., Adams, M. B., Wiley, J. D., Whitehead, R. F., Avery, G. B., Mullaugh, K. M., and Mead, R. N.: Short term temporal variability in the photochemically mediated alteration of chromophoric dissolved organic matter (CDOM) in rainwater, Atmos. Environ., 50, 112-119, http://dx.doi.org/10.1016/j.atmosenv.2011.12.054, 2012.*
- ➢ *Vodacek, A., Blough, N. V., DeGrandpre, M. D., Peltzer, E. T., and Nelson, R. K.: Seasonal Variation of CDOM and DOC in the Middle Atlantic Bight: Terrestrial Inputs and Photooxidation, Limnol. Oceanogr., 42, 231-253, http://dx.doi.org/10.1117/12.26643, 1997.*

We have added the citations about aerosol, for example,

- ➢ *Budisulistiorini, S. H.; Riva, M.; Williams, M.; Chen, J.; Itoh, M.; Surratt, J. D.; Kuwata, M.: Light-Absorbing Brown Carbon Aerosol Constituents from Combustion of Indonesian Peat and Biomass. Environ. Sci. Technol., 51, 4415-4423, http://dx.doi.org/10.1021/acs.est.7b00397, 2017.*
- ➢ *Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; Jenkin, M. E.; Rossi, M. J.; Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II - gas phase reactions of organic species, Atmos. Chem. Phys., 6, 3625-4055, http://dx.doi.org/10.5194/acp-6-3625-2006, 2006.*
- ➢ *Carlton, A. G.; Turpin, B. J.; Altieri, K. E.; Seitzinger, S.; Reff, A.; Lim, H. J.; Ervens, B.: Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous photooxidation experiments, Atmos. Environ., 41, 7588-7602, http://dx.doi.org/10.1016/j.atmosenv.2007.05.035, 2007.*
- ➢ *Claeys, M.; Graham, B.; Vas, G.; Wang, W.; Vermeylen, R.; Pashynska, V.; Cafmeyer, J.; Guyon, P.; Andreae, M. O.; Artaxo, P.; Maenhaut, W.: Formation of secondary organic aerosols through photooxidation of isoprene, Science, 303, 1173-1176, http://dx.doi.org/10.1126/science.1092805, 2004.*
- ➢ *Mang, S. A.; Henricksen, D. K.; Bateman, A. P.; Andersen, M. P. S.; Blake, D. R.; Nizkorodov, S. A.: Contribution of Carbonyl Photochemistry to Aging of Atmospheric Secondary Organic Aerosol, J. Phys. Chem. A, 112, 8337-8344, http://dx.doi.org/10.1021/jp804376c, 2008.*

3. Line 42: A lot of the cited references are not specific to aerosols and have been used for aquatic CDOM. This is misleading and is a false statement.

According to the reviewer's suggestion, we have corrected the references. Details are shown in second comment.

4. Line 62: super oxide and not super-oxygen and hydroxyl radicals and not hydroxyl

According to the reviewer's suggestion, we have corrected "*hydroxyl (•OH)*" to "*hydroxyl radicals (•OH)*" in improved paper.

For example, we added "*COM can be oxidized by hydroxyl radicals (•OH)*" in improved paper.

5. Line 91-92: At 500 C, the combustion of organics is supposed to be complete, especially by introducing fresh air, I remain confused why this was done. Also, how do you get POA after achieving complete combustion as it was stated in the text?

POA samples in the study is not the residue after complete combustion, but the particulate matter generated in the combustion process. Even if the temperature rises to 500 °C, there will be a lot of particulate matter. The combustion process is dynamic and particulate matter generated during the combustion process would be diluted and cooled in the mixing box (Figure S1). As shown in the figure, POA was collected on quartz filters.

6. Line99-108: The description of the reactor system is highly confusing and even the photos do not help to clarify the setup.

According to the reviewer's suggestion, we have revised the description of the reactor.

(1) we have corrected "*Two air vents was used to air exchange and Two water cycle vents were connected to water circulator to ensure that the temperature constant in the reactor*" to "*Two air vents were designed in upper side of reactor. Two water cycle vents were designed in lower side and connected with water circulator to keep temperature was about 25°C in the reactor*" in improved Supporting Information.

(2) We have added "*Two capsules (Figure S2(b) & (c) of SI) were designed for triplet state and ROS generation experiment*" in Sec 2.2 in improved paper.

(3) We have corrected the figure and added the figure in improved Supporting Information.

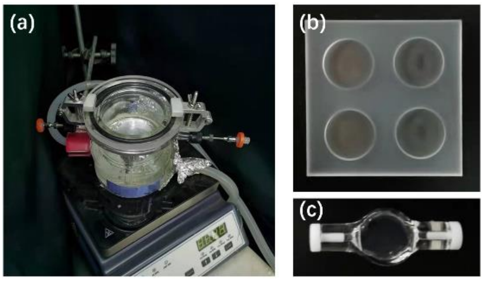
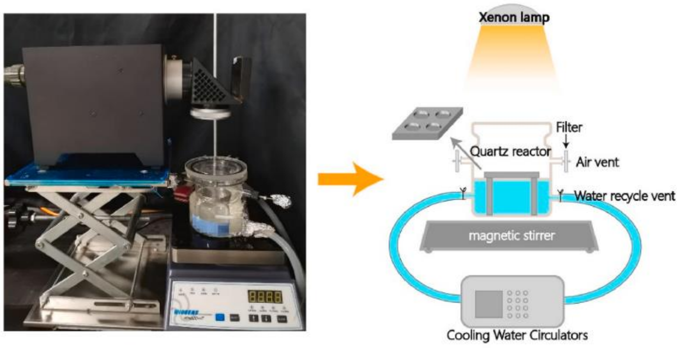


Figure S2. *Schematic diagrams of the photochemical devices. (a) The reactor is used for maintaining the reaction environment. (b) The capsule is used for the experiment of triplet state inducing singlet oxygen. The size of quartz plate is 35×35 mm^2. The size of the tanks is a radius of 5.6 mm and a depth of 2.5 mm. (c) The capsule is used for triplet state experiments. The reactor is made of quartz. The plugs are made of Teflon. The internal volume is 200 μL.*

The details of reactor could refer to our previous study.



Photochemistry reaction device. The inside diameter of the reactor is approximately 11 cm, and the height is approximately 18 cm. The reactor is connected to a cooling-water circulator to ensure that the water temperature in the reactor was constant and the water temperature is set to 8 ℃ (Chen et al. 2021).

- *Chen, Q.; Mu, Z.; Xu, L.; Wang, M.; Wang, J.; Shan, M.; Fan, X.; Song, J.; Wang, Y.; Lin, P.; Du, L.: Triplet-state organic matter in atmospheric aerosols: Formation characteristics and potential effects on aerosol aging, Atmos. Environ., 252, 118343, https://doi.org/10.1016/j.atmosenv.2021.118343, 2021.*

7. Line 125-130: How was organic carbon quantified here? It is not clear at all.

The extracts were analyzed by the OC/EC analyzer.

We have revised section 2.4. Section 2.3 and 2.4 were merged. We have corrected "*The method of organic carbon (OC) analysis could refer to the previous literature. 100 μL extracts were injected on the baked quartz filter (Mu et al., 2019). Then, the wet filters were dried out by a rotary evaporator and the WSOC/WISOC adhered to the filter. Carbonaceous components on the filters were analyzed by the OC/EC online analyzer*" to "*The analytical method of carbonaceous components has been described previously (Mu et al., 2019). Briefly, 100 μL extracts were injected on the baked quartz filter. Then, the wet filters were dried out by a rotary evaporator and the dried filters were analyzed by the OC/EC online analyzer*" in section 2.3 in improved paper.

8. Line 138: Optical properties are highly dependent on the matrix and it is not expected to be able to directly compare EEMS obtained in methanol versus the one collected in water. It is even more problematic when the dataset is combined to create a PARAFAC model.

In order to compare the differences of fluorescence components in water-soluble and water-insoluble organic matter, we coupled the water-soluble and water-insoluble components to establish the model. Similar methods have been proved in our previous study (Chen et al., 2021). Chen et al. (2016) compared EEMs of water-soluble and water-insoluble BrC. The result has suggested that solvent had no significant effect on the EEM spectra of complex mixtures in aerosols.

We have stated "*based on the Chen's studies (2020; 2016b), water-soluble and water-insoluble samples were combined to create the PARAFAC model to illustrate the distribution of fluorophores in WSOM and WISOM and solvent had no significant effect on the EEMs of complex mixtures in aerosols*" in Sec 3.2 in improved paper.

- *Chen, Q. C.; Li, J. W.; Hua, X. Y.; Jiang, X. T.; Mu, Z.; Wang, M. M.; Wang, J.; Shan, M.; Yang, X. D.; Fan, X. J.; Song, J. Z.; Wang, Y. Q.; Guan, D. J.; Du, L.: Identification of species and sources of atmospheric chromophores by fluorescence excitation-emission matrix with parallel* *factor analysis, Sci. Total Environ., https://doi.org/10.1016/j.scitotenv.2020.1373222020, 718, 10, 2020.*

- *Chen, Q. C.; Ikemori, F.; Mochida, M.: Light Absorption and Excitation–Emission Fluorescence of Urban Organic Aerosol Components and Their Relationship to Chemical Structure. Environ. Sci. Technol., 50, 10859-10868, https://doi.org/10.1021/acs.est.6b02541, 2016.*

9. Line 146L It still does not state here what triplet state species is referred to.

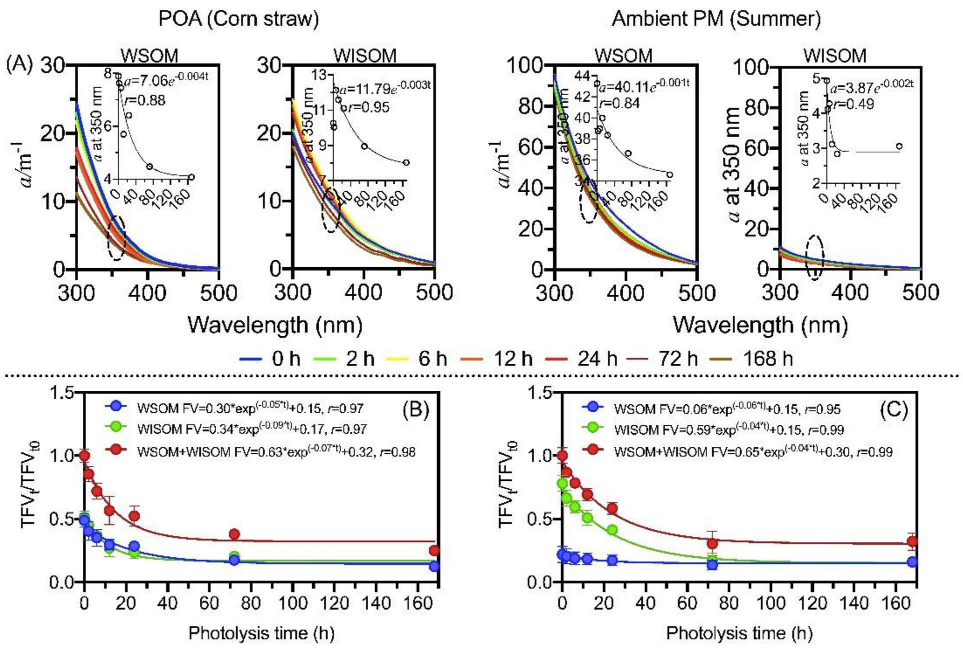
Triplet states is important reactive intermediates and it could induce the ROS. Therefore, ^{3}COM* may affect photochemical process.

We have corrected "*The triplet states generation ability before and after photolysis were studied*" to "*As short-lived reactive intermediates, ^{3}COM* have an important impact on photochemical process in atmospheric environment (Kaur et al., 2018). Therefore, ^{3}COM* generation ability before and after photodegradation were studied*" in Sec 2.5 in improved paper.

We have revised "*Aromatic ketones could be excited to generate triplet state (^{3}COM*) under light conditions (Rosario-Ortiz and Canonica, 2016; Del Vecchio and Blough, 2004; Wenk et al., 2013; Ma et al., 2010). ^{3}COM* induce reactive oxygen species (ROS), such as singlet oxygen ($^1O_2$), super-oxygen (•O_2^-) and hydroxyl (•OH), which could drive aerosol aging (Paul Hansard et al., 2010; Szymczak and Waite, 1988; Zhang et al., 2014; Rosario-Ortiz and Canonica, 2016; Sharpless, 2012; Haag and Gassman, 1984)*" to "*Upon light absorption, high-energy singlet state COM (^{1}COM*) could be generated. ^{1}COM* deactivate quickly with the ways of emitting photon (fluorescence) and intersystem crossing (triplet state, ^{3}COM*). ^{3}COM* can generate reactive oxygen species (ROS), such as singlet oxygen ($^1O_2$), super oxide (•O_2^-) and •OH, which indicate that ^{3}COM* play a critical role in ROS formation and pollutant attenuation (Paul Hansard et al., 2010; Szymczak & Waite, 1988; Zhang et al., 2014; Rosario-Ortiz and Canonica, 2016; Sharpless, 2012; Haag and Gassman, 1984; Zhou et al., 2019). A lot of DOM, such as aromatic ketones (Canonica et al., 2006; Marciniak et al., 1993), benzophenone (Encinas et al., 1985), and phenanthrene (Wawzonek & Laitinen, 1942), have been identified as the precursor of ^{3}COM**" in Sec 1 in improved paper.

10. Figure 4: Absorbance should be normalized to pathlength. Please see Helms, J. R.; Stubbins, A.; Ritchie, J. D.; Minor, E. C.; Kieber, D. J.; Mopper, K., Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. Limnology and Oceanography 2008, 53, (3), 955-969. And equation (2) within.

According to the reviewer's suggestion, we have corrected Fig.4 (Fig.2 in improved paper).



We have added the equation in Supporting Information.

“*Absorption coefficient is calculated as follows (Helms et al., 2008):*

$$a=2.303A/l \tag{4}$$

In (4), a is absorption coefficient (m^{-1}), A is absorbance, and l is path length (m)”.

- *Helms, J. R.; Stubbins, A.; Ritchie, J. D.; Minor, E. C.; Kieber, D. J.; Mopper, K.: Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter, Limnol. Oceanogr., 53, 955-969, https://doi.org/10.4319/lo.2008.53.3.0955, 2008.*

Referee #2

The manuscript 'Photodegradation of Atmospheric Chromophores: Changes in Oxidation State and Photochemical Reactivity' provides results on the photochemical aging of atmospheric aerosols (both ambient PM and laboratory generated POA). The results include OC/EC analysis, parallel factor (PARAFAC) analysis of excitation-emission matrices, and photosensitization of 1O2 with each measured as a function of solar irradiation. The manuscript has been improved but still requires refinement in the writing/presentation and explanation. My comments are outlined below. Major comments:

We appreciate the positive comments from reviewer. According to the reviewer's comments, we have revised this paper. The details are as follows. *The blue italics are comments of reviews. The red italics are improvements and original text of reviews.* The black font are responses.

1) In the first paragraph of section 3.1, the authors go back and forth between water-soluble and water-insoluble organic matter and WSOC and WISOC. Is there a reason the terminology is different? In Line 184-186, I believe the authors mean to say that the WISOC decomposes more rapidly in ambient PM than in POA. If so, rephrase accordingly. In addition, the authors say that ambient PM has been subjected sufficient atmospheric oxidation so that OM is not decomposed, however, the WISOC fraction of ambient PM shows significant attenuation after photolysis. These two aspects seem at odds with one another. More explanation of what the attenuation ratio is would be instructive. This doesn't appear in Sec. 2.4 of the Methods or in Sec. 3.1.

WSOM and WISOM are defined as extracted organic matter. WSOC and WISOC are defined as carbonaceous component in extracted organic matter.

(1) We have corrected the terminology in Sec 3.1 and we have revised the sentence.

We have corrected "*The results show that both water-soluble and water-insoluble organic matter undergo partial photolysis in POA samples (Fig.3A), with an average decrease of 22.1% and 3.5%, respectively*" to "*In POA, water soluble and water insoluble organic carbon (WSOC and WISOC) decrease by 22.1% and 3.5%, respectively.*" in Sec 3.1 in improved paper.

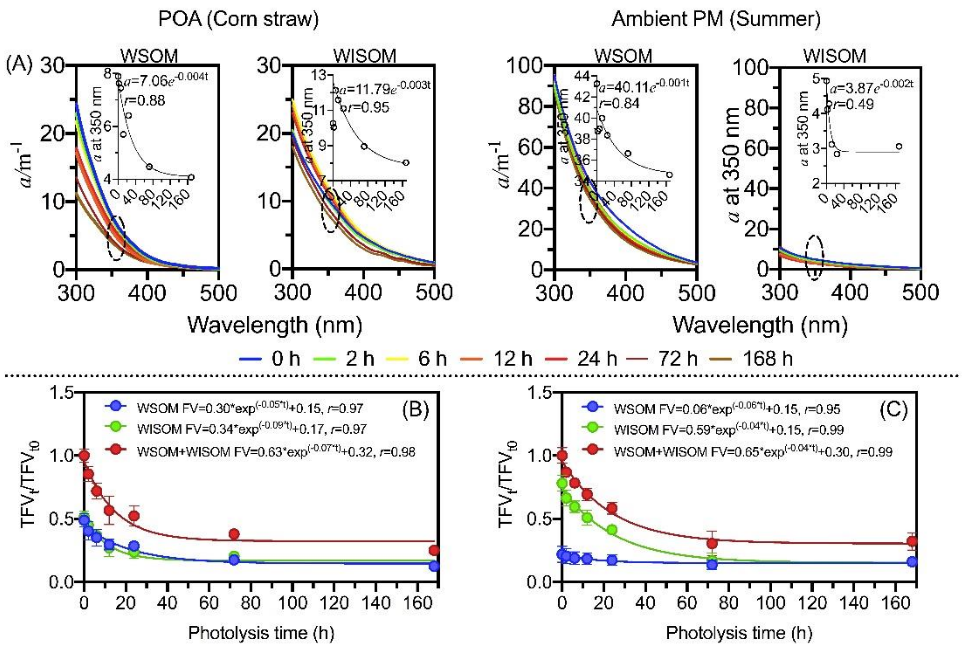
(2) We have added more explanation in Sec 3.1.

For example, we have added "*there is a process of OC1 translating into pyrolysis carbon (OPC)*" in Sec 3.1 in improved paper.

We have corrected "*The result reflects that different carbonaceous components have the similar abilities of photodegradation in ambient PM. Organic matter with high molecular weight is photocomposed to small molecular weight and the molecular weight tend to be consistent following the photodegradation*" in Sec 3.1 in improved paper.

2) In Sec. 3.2, Lines 202-206 are very repetitive stating that the absorbance decreases significantly during photolysis in multiple consecutive sentences. Re-write for clarity. Also in this paragraph, the authors state that the absorbance decay is inconstant and cannot be mathematically analyzed. Do the authors mean that the absorbance decrease cannot be fit to a single exponential decay? Can the authors report a total percent decrease in the absorbance at 350 nm instead?

The attenuations of absorption coefficients are fit to first-order decay and we have revised Fig.4 (Fig.2 in improved paper).



We have corretcd “*Both absorbance and total fluorescence volume (TFV, RU-nm2/m3) significantly decrease during aerosol photolysis (Fig.4). Changes in optical properties are shown in Figure S3, S4 and S5. The decrease of absorbance confirm that COM are photo-bleached (Duarte et al., 2005) and the decay function of photolysis on absorbance is significant (Aiona et al., 2018). As shown in the scatter plot (**Fig.4**), absorbance decreases significantly during photolysis*” to “*As shown in Fig.2, both absorption coefficients and total fluorescence volume (TFV, RU-nm2/m3) significantly decrease following aerosol photodegradation, which suggest that COM are photo-bleached (Aiona et al., 2018; Duarte et al., 2005; Liu et al., 2016). The attenuations of fluorescence and absorption coefficients are fit to first-order decay. The absorption coefficients decrease by 32.0% and TFV decreases by 71.4% on average*.” in Sec 3.2.

3) As mentioned above the authors claim that the ambient PM samples have been subjected to sufficient atmospheric oxidation (line 196), however in Figure 5C, these samples are dominated by low oxidation HULIS/C2 (especially compared to the POA samples). How do you reconcile these two observations?

(1) The components of ambient PM are affected by various sources and atmospheric chemical processes, including secondary aerosol. The main components are water-insoluble and amino acid fluorophores in POA. However, the content of amino acid-like fluorophores in ambient PM is lower than that in POA, which suggest that the amino acid-like fluorophores have been photodegraded or transformed into HULIS fluorophores in ambient aerosol.

(2) Low oxidation HULIS could be converted into high oxidation HULIS in ambient PM. The result confirms the conclusion.

4) In the paragraph starting at Line 274, the authors begin using the term ‘light excitation’ instead of photolysis or illumination which are used in the figures. It would improve the manuscript to make this terminology consistent. Also, in Line 280-281, what is meant by ‘POA has certain oxidability’? Re-phrase whatever concept is trying to be conveyed here.

We corrected “*light excitation*” to “*illumination*” in Sec 3.3 in improved paper.

We have deleted "*POA has certain oxidability*" to "*which suggest POA could generate* $^1O_2$ *without illumination*" in improved paper.

5) The Implications section is still brief and lacks any reference to previous literature. This section could also be improved by broader interpretation of all the included results. For instance, how do the results in Sec. 3.3 on singlet oxygen generation connect with the results on degree of oxidation in Sec. 3.1 and 3.2, i.e. photolysis increases the degree of oxidation in the aerosol samples which in turn leads to a higher capacity for singlet oxygen formation via photosensitization reactions.

We have revised Implications.

"*We made a comprehensive study in COM photo-degradation and the effect of COM photo-degradation on optical properties, chemical compositions, and photochemical activity. The characteristics of COM photo-degradation were revealed. COM photodegradation could result in reduction of carbonaceous components, attenuation of optical properties, and changes in components. We also propose that the COM photodegradation should be evaluated from the three aspects for further study. (1) The impact of COM photodegradation on carbonaceous content are unclear. Previous studies have revealed that WSOC did not significantly change in the river DOM (Gonsior et al., 2009) and 0.2% of DOC was mineralized (Tranvik et al., 1998). However, the observation in the study suggests that changes in carbonaceous component is different in aerosols, which could be attributed to the differences in original components. (2) Decreasing in optical properties is significant. Absorption coefficient and fluorescence intensity can be thought of as a tracer for molecular weight (Stewart & Wetzel, 1980). Therefore, optical properties could indicate the changes in molecular weight of COM during the photodegradation process. The characteristic could be suitable for exploring the impact of photodegradation on COM components. (3) Photodegradation of COM may dominant the fluorophores components (Aiona et al., 2018; Timko et al., 2015). High-molecular-weight COM could be decomposed into low-molecular-weight COM during photodegradation process. The conversion of low-oxidation HULIS to high-oxidation HULIS is observed. Changes in COM may represent the degree of organic substances oxidation. Therefore, we suggested that optical parameter and degree of oxidation of organic molecules should be use for characterizing the aerosol photo-aging process (Maizel et al., 2017).*

Photodegradation can not only change the properties and components of COM, but also change their photochemical activity, which furtherly has a potential impact on the aerosol fate. Photodegradation and/or conversion of COM could be considered to be the main influence factor for photochemical reaction capacity (McNight et al., 2001; Zepp et al., 1985). Photochemical activity was quantified by the yield of triplet state and 1O2. However, two different methods, two different results. COM photodegradation can restrain $^1O_2$ *generation but the effect of photodegradation on 3COM* are unclear. Photodegradation has a significant inhibiting effect on the* $^1O_2$ *yield in aerosols (Latch et al. 2006; Chen et al., 2018). We insist that aerosol aging would be changed by photodegradation due to the yield of* $^1O_2$ *is changed. Changes in triplet state generation are uncertain in ambient PM and POA. There are two reasons for it. On the one hand, only a small amount of COM are the precursor of* $^3COM^*$ *in aerosols. On the other hand, the energy* *of capturing agents was closely related to ^{3}COM* quantification and ^{3}COM* could not be captured completely. Other capturing agents may lead to different results. Thus, ^{3}COM* could not properly illustrate photo-degradation. COM photodegradation would be play an important role in the content of ROS and ROS could celebrate the COM photooxidation (Claeys et al., 2004). Given the results, the interaction effect is significant in aerosol.*

In summary, atmospheric photochemistry process has a remarkable impact on aerosol aging. Prediction of atmospheric lifetime and improvement of quality are strongly associated with photochemistry. We prove that carbonaceous content, absorption coefficients, fluorescence intensity, and photochemical activities are useful to reflect COM photodegradation process and aerosol fate. In addition, COM photodegradation have different impact on chemical activity in different aerosols, which may have different mechanisms. Therefore, the mechanisms of COM photodegradation effecting aerosol photo-aging deserve further investigation.".

We have added references in Sec 4. For example,

- *Gonsior, M., Peake, B. M., Cooper, W. T., Podgorski, D., D'Andrilli, J., and Cooper, W. J.: Photochemically induced changes in dissolved organic matter identified by ultrahigh resolution fourier transform ion cyclotron resonance mass spectrometry, Environ. Sci. Technol., 43, 698-703, http://dx.doi.org/10.1021/es8022804, 2009.*
- *Tranvik, L.; Kokalj, S.: Decreased biodegradability of algal DOC due to interactive effects of UV radiation and humic matter, Aquat. Microb. Ecol., 14, 301-307, https://doi.org/10.3354/ame014301, 1998.*
- *Stewart, A. J.; Wetzel, R. G: Fluorescence: absorbance ratios—a molecular-weight tracer of dissolved organic matter, Limnol. Oceanogr., 25, 559-564, https://doi.org/10.4319/lo.1980.25.3.0559, 1980.*
- *Aiona, P. K., Luek, J. L., Timko, S. A., Powers, L. C., Gonsior, M., and Nizkorodov, S. A.: Effect of Photolysis on Absorption and Fluorescence Spectra of Light-Absorbing Secondary Organic Aerosols, ACS Earth Space Chem., 2, 235-245, 10.1021/acsearthspacechem.7b00153, 2018.*

Minor Comments:
Line 2: Change 'photosensitiveness' to 'photosensitivity' and 'have' to 'has'
We have corrected "*photosensitiveness*" to "*photosensitivity*" and "*have*" to "*has*".

Line 10-13: Re-write this sentence: 'In terms of photochemical reactivity, the triplet state COM decreases slightly in ambient particulate matter samples but increases in primary organic aerosol (POA) following photolysis.
We have corrected "*In terms of photochemical reactivity, compared with before photolysis, the triplet state COM (3COM*) decrease slightly in ambient particulate matter (ambient PM) samples, but increase in primary organic aerosol (POA)*" to "*COM Photodegradation has a significant impact on photochemical reactivity. The content of triplet state COM decreases slightly in ambient particulate matter but increases in primary organic aerosol following photodegradation*".

Line 25: Change 'chemistry' to 'chemical'

We have corrected "*secondary chemistry reactions*" to "*secondary aerosols*".

Line 39-40: Change 'not complete clear' to 'unclear'
We have deleted "*Yet the mechanisms of photo-bleaching process are still not complete clear*".

Line 58: Change 'participate' to 'participates'
We have corrected "*participate*" to "*participates*".

Line 60: Change '' to 'solar irradiation'
We have corrected "*Aromatic ketones could be excited to generate triplet state (3COM*) under light conditions (Rosario-Ortiz and Canonica, 2016; Del Vecchio and Blough, 2004; Wenk et al., 2013; Ma et al., 2010)*" to "*such as aromatic ketones (Canonica et al., 2006; Marciniak et al., 1993), benzophenone (Encinas et al., 1985), and phenanthrene (Wawzonek & Laitinen, 1942), have been identified as the precursor of* ^{3}*COM**".

Line 61: Change 'induce' to 'can generate'
We have corrected "^{3}*COM* induce reactive oxygen species (ROS)*" to "*COM participates in atmospheric photochemistry process indirectly through generating reactive intermediates*".

Line 76: Change 'stated' to 'studied'
We have corrected "*The effects of COM on photochemical reactivity and aerosol aging (photochemical reactivity is characterized by triplet state and singlet oxygen generation capacity) are also stated by the method of reactive species capture technology and electron paramagnetic resonance spectrometer (EPR)*" to "*to investigate the effects of COM photo-degradation on photochemical reactivity and aerosol aging (photochemical reactivity is characterized by triplet state and singlet oxygen generation capacity)*".

Line 125: Change 'could refer to the previous literature' to 'has been described previously'
We have corrected "*The method of organic carbon (OC) analysis could refer to the previous literature*" to "*The analytical method of carbonaceous components has been described previously*".

Line 146 Change 'states' to 'state'
We have corrected "*triplet states*" to "^{3}*COM**".

Line 229: Change 'study' to 'studied' and 'chromophores' to 'fluorophores' to highlight that you are referring to fluorescence here
We have corrected "*Tang et al. (2020) study the chromophores in water-soluble and water-insoluble samples, respectively*" to "*Although previous study analyzed the water-soluble and water-insoluble fluorophores separately*".

Line 230: Change ', respectively' to 'separately'
We have corrected "*Tang et al. (2020) study the chromophores in water-soluble and water-insoluble samples, respectively*" to "*Although previous study analyzed the water-soluble and water-insoluble fluorophores separately*".

Line 231: Change ‘so that’ to ‘to’

We have corrected “*so that*” to “*to*”.

Line 232: Change ‘chromophores’ to ‘fluorophores’

We have corrected “*chromophores*” to “*fluorophores*”.

Line 238: Rewrite as “The composition of the fluorophores changes significantly during the photolysis process.”

We have corrected “*The compositions of chromophores change significantly during photolysis process*” to “*The content of fluorophores changes significantly during the photodegradation process*”.

Line 260: Change ‘states’ to ‘state’

We have corrected “*states*” to “*state*”.

Line 263 Change ‘not as expected’ to ‘unexpected’

We have corrected “*not as expected*” to “*unexpected*”.

Line 274: Change to ‘further induce singlet oxygen formation’

We have corrected “*COM can generate triplet states and furtherly induce singlet oxygen*” to “*COM can generate triplet state and further generate singlet oxygen*”.

Line 278: Change ‘is’ to ‘of’

We have corrected “*is*” to “*of*”.