Response for acp-2020-1223

Anonymous Referee #1 (reconsidered after major revisions)

The manuscript remains difficult to read due to grammatical errors, I started to correct them, but there are too many and this should have been checked by the authors. The discussion on water-soluble and insoluble fractions is still very confusing and the insoluble fraction is a methanolic extract. Was the methanolic extract irradiated? If so fundamental differences are expected due to the solvent. While the manuscript states that no significant changes between solvents were observed, this cannot be assumed during photodegradation experiments at all! What is the justification to call statistical components for the PARAFAC analysis low oxidation HULIS or high-oxidation HULIS? PARAFAC components have no chemical meaning and are solely derived from a statistical modelling. If such assumptions are made, they need to be defined by correlations with other analytical techniques that determine oxygenation levels or increases in oxygen-containing functional groups.

We appreciate the comments from reviewer. According to the reviewer's comments, we have carefully revised this paper. Especially, we have further modified grammatical errors in the whole paper. The details changes 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. We have corrected grammatical errors in the whole paper. For example,

(1) We have revised "*Photodegradation of precursors limit singlet oxygen generation and affect the aerosol photochemistry process. In conclusion, COM photodegradation not only change the compositions and properties, but also change aerosol aging*" to "*The combination of optical property, chemical component, and reactive oxygen species have an important impact on the atmosphere quality. The new insights on photodegradation of COM in aerosol reinforce the importance of studying DOM related with the photochemistry and aerosol aging*" in line 14-17 in the improved paper.

(2) We have revised "*^{3}COM* can generate reactive oxygen species (ROS)*" to "*^{3}COM* not only can produce photochemical reaction directly, but also can generate reactive oxygen species (ROS)*" in line 63-64 in the improved paper.

(3) We have revised "*Fig.4 show the difference of triplet state generation before and after the photodegradation*" to "*Fig.4 shows the variation of triplet state generation before and after the photodegradation*" in line 270-271 in the improved paper.

(4) The more changes are presented in the track-change-mode version of the manuscript. For example, L1, L5, L33, L43, L49, L66, L70, L80, L95, L126, L140, L169, L190, L209, L233, L304, L311, L320, L331, L356, L399, L408, and so on.

2. We have refined the extraction section in the improved paper.

Firstly, organic matter on the filter was extracted by water and the water-soluble organic matter (WSOM) was obtained. Secondly, residual organic matter on the filter was further extracted by methanol and we obtain the methanol-soluble organic matter (MSOM). Noted that only WSOM was used in the triplet state and singlet state experiment.

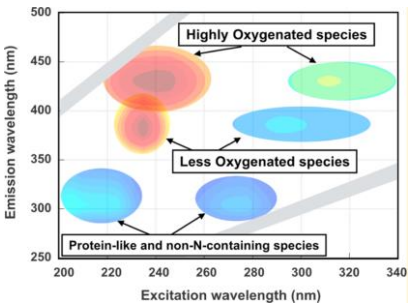
We have stated "*The samples with the photodegradation time of 0 and 7 d were defined as the original and photolyzed samples, respectively. Only WSOM of original and photolyzed samples was*

used in the triplet state generation experiment. A capsule (Figure S2(c)) was designed for this experiment" in line 143-146 and "*Only WSOM of original and photolyzed was used in the singlet oxygen generation experiment*" in line 162-163 in the improved paper.

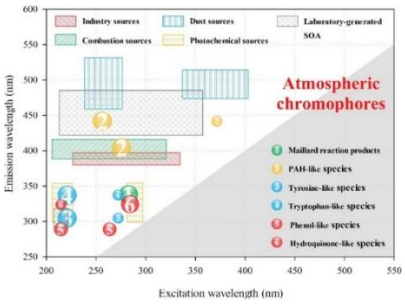
3. EEMs could not reveal the chemical structure on the molecular level of complex fluorophores, but it can represent the overall fluorophores structure such as the chromophore types (Murphy et al., 2013; Chen et al., 2020, 2021a and b). The COM was identified as high-oxidation HULIS or low oxidation HULIS, which is based on previous research by Chen et al (2016). They result suggests that these fluorophores have similar fluorescent functional groups and structures with high-oxidation or low oxidation ion fragments in HR-AMS. The result does not reveal that theses fluorophores must be high-oxidation or low oxidation organic compounds. EEM is a holistic approach to characterize complex COM in the environment.

We also stated that "*Pyrolysis carbon is identified as oxygen-containing organic substance. Thus, the increasing oxygen-containing organic matter may be due to the photo-inducing oxidation reaction*". The results suggest the effect of photooxidation on COM.

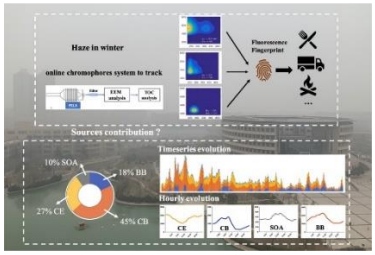
EEM is an important method for directly characterizing the occurrences, origins, and chemical behaviors of atmospheric chromophores. Examples are as follows.



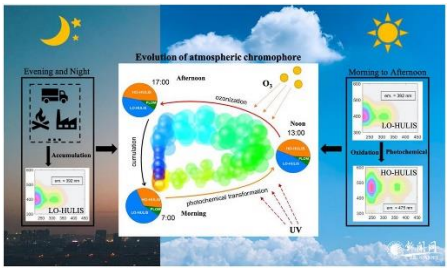
EEM can identify the overall chemical structure of complex fluorophores (Graphical abstract, Chen et al., 2016).



EEM can identify the chemical structure and origins of complex fluorophores (Graphical abstract, Chen et al., 2020).



EEM can identify the origins of complex fluorophores (Graphical abstract, Chen et al., 2021a).



EEM can tracer the degree of oxidation of complex fluorophores (Graphical abstract, Chen et al., 2021b).

- *Murphy, K. R., Stedmon, C. A., Graeber, D., et al.: Fluorescence spectroscopy and multi-way techniques. PARAFAC, Anal. Methods 2013, 5, 6557-6566.*
- *Chen, Q., Hua, X., Li, J., et al.: Identification of species and sources of atmospheric chromophores by fluorescence excitation-emission matrix with parallel factor analysis. Science of the total environment 2020, 718, 137322.*
- *Chen, Q., Hua, X., Li, J., et al.: Diurnal evolutions and sources of water-soluble chromophoric aerosols over Xi'an during haze event, in Northwest China. Science of the total environment 2021a, 786, 147412.*
- *Chen, Q., Hua, X., Dyussenova, A., et al.: Evolution of the chromophore aerosols and its driving factors in summertime Xi'an, Northwest China. Chemosphere 2021b, 281, 130838.*
- *Chen, Q., Miyazaki, Y., Kawamura, K., et al.: Characterization of chromophoric water-soluble organics in an urban, a forest, and the eastern equatorial Pacific aerosols using EEM and HR-ToF-AMS spectroscopy. Environ. Sci. Technol., 2016, 50, 10351-10360.*

Some specific comments:

1. Line 14: precursors of what?

We have revised "*Photodegradation of precursors limit singlet oxygen generation and affect the aerosol photochemistry process*" to "*which could be attributed to photodegradation of precursors of $^1O_2$*" in line 14 in the improved paper.

2. Line 35: add "that" to "….due to chromophores that are photo-bleached in aerosols"

We have revised "*due to chromophores are photo-bleached in aerosols*" to "*that due to COM is photo-bleaching in aerosol*" in line 36 in the improved paper.

3. Line 36: secondary and not second

We have revised "*second organic aerosol (SOA)*" to "*secondary organic aerosol (SOA)*" in line 40 in the improved paper.

4. Line 37: define MAC

We have defined "*mass absorption coefficents (MAC)*" in line 37 in the improved paper.

We have revised "*Lee et al. (2014) reported that the mass absorption coefficents (MAE)*" to "*Lee et al. (2014) also reported that the MAC*" in line 39 in the improved paper.

5. Line 38: define OM

We have revised "*wood-burning OM*" to "*wood-burning organic matter (OM)*" in line 38 in the

improved paper.

6. Line 39: hydroxyl groups cannot be photodegraded. You might want to say hydroxylated aromatic phenols.

We have revised "*hydroxyl groups*" to "*hydroxylated aromatic phenols*" in line 39 in the improved paper.

7. Line 49: define POA

We have revised "*POA*" to "*primary organic aerosol (POA)*" in line 49 in the improved paper.

8. Line 52: comprehensively and not comprehensive

We have revised "*comprehensive*" to "*comprehensively*" in line 52 in the improved paper.

9. Line 55: What is the complex photochemical reaction?

Extensive research has been done in COM photochemical reaction, such as generating reactive oxygen species, photo-Fenton reaction, and the formation of complexation of the metal ions with COM.

We have revised "*Atmospheric COM could participate in the complex photochemical reaction, which further affect the aerosol aging*" to "*Photochemical process of COM largely determines the aerosol aging*" in line 54 in the improved paper.

10. Line 66: triplet state COM can also directly react and not just via ROS.

We have revised "*^{3}COM* can generate reactive oxygen species (ROS)*" to "*^{3}COM* not only can produce photochemical reaction directly, but also can generate reactive oxygen species (ROS)*" in line 64 in the improved paper.

11. Line 73-74: rephrase, this is grammatically confusing

We have revised "*Why ^{3}COM* is employed not ^{1}COM*? The reasons are lower formation rate (15–100 times slower than ^{1}COM*), lower quenching rate (20000 times lower than ^{1}COM*), and highter steady-state concentrations of ^{3}COM* (200~1300 times higher than ^{1}COM*)*" to "*Compared with ^{1}COM*, the characteristics of ^{3}COM* are lower formation rate (15–100 times slower than ^{1}COM*), lower quenching rate (20000 times lower than ^{1}COM*), and higher steady-state concentration (200~1300 times higher than ^{1}COM*)*" in line 72-75 in the improved paper.

12. Line 112: Please further define this fraction, while it is unsoluble in water it is still soluble in methanol. Water insoluble fraction could otherwise be mistaken for all the particulate COM, which is not the case. Why not calling it methanolic fraction after define it as being the fraction without the water-soluble components?

Firstly, organic matter on the filter was extracted by water and the water-soluble organic matter was obtained. Secondly, residual organic matter on the filter was further extracted by methanol and we obtain the methanol-soluble organic matter.

We have revised "*water-insoluble organic matter (WISOM)*" to "*methanol-soluble organic matter (MSOM)*" in the improved paper.

13. Line 117. I still would briefly describe what was done and not solely referring to previous publications.

We have described the method of OC/EC measurement in line 116-124 in the improved paper.

We added "*Organic carbon (OC) was measured in the absence of oxygen. An oven in the instrument was filled with helium and temperature was risen in a gradient style. Different temperatures are needed for particular analysis phases (OC1-310 ℃, OC2-472 ℃, OC3-615, OC4-850 ℃). Element carbon (EC) was measured in the present of oxygen. The oven in the instrument was filled with helium-oxygen gas mixture (He/O_2=10/1). Different temperatures were also needed for particular analysis phases (EC1-550 ℃, EC2-625 ℃, EC3-700℃, EC4-775 ℃, EC5-850 ℃, EC6-870 ℃). The products in the heating process were further oxidized to CO_2. The carbon content was obtained through the measurement of CO_2*" in line 116-124.

14. Line 124: not exposure time. This is integration time.

We have revised "*The exposure time was 0.5 s*" to "*The integration time was 0.5 s*" in line 130 the improved paper.

15. Line 128: define PARAFAC and explain that a model was created from 111 samples. It sounds like you used somebody else's model but that is not the case, is it?

We have revised "*The EEM data was analyzed by parallel factor analysis mode*" to "*The EEM data was analyzed by parallel factor analysis model (PARAFAC)*" in line 134 the improved paper.

PARAFAC has already been used widely in identifying fluorophores and PARAFAC model has been described in previous study (Murphy et al., 2013). The program was public.

- *Murphy, K. R., Stedmon, C. A., Graeber, D., et al.: Fluorescence spectroscopy and multi-way techniques. PARAFAC, Anal. Methods 2013, 5, 6557-6566.*

16. Line 132: You need to explain better why the 4-component model was selected and not any other.

According to the EEM characteristics and the residual error variation trend of the 2-7 component PARAFAC models, 4 fluorescent components were identified. In the parallel factor analysis, the most appropriate number of components can be selected by judging the EEM characteristics and model residuals (Figure S4). In general, the smaller the sum of squared residuals and the ascensional range, the better the fitting effect, but increasing the number of components will add the difficulty of explanation. All things considered, the 4-component PARAFAC model is more appropriate.

17. Line 183: I do not understand why it is claimed here that WSOC is completely photodegraded. Where is the evidence?

We have revised "*The EEM data was analyzed by parallel factor analysis mode*" to "*OM has been photodegraded adequately*" in line 193 the improved paper.

WSOC is nearly unchanged. POA is fresh and ambient PM has undergone long-term aerosol aging. Therefore, we stated that "*OM has been photodegraded adequately*" in real environment.

18. Line 236: PARAFAC components are statistically defined and hence do not have any chemical meaning. They are solely derived from the variations within a dataset. It is not at all clear how the oxidation level can be inferred on statistical components. On what kind of supporting data is this based?

EEMs could not reveal the chemical structure on the molecular level of complex fluorophores, but it can represent the overall fluorophores structure such as the chromophore types (Murphy et al., 2013; Chen et al., 2020, 2021a and b). The COM was identified as high-oxidation HULIS or low oxidation HULIS, which is based on previous research by Chen et al (2016). They result suggests that these fluorophores have similar fluorescent functional groups and structures with high-oxidation or low oxidation ion fragments in HR-AMS. The result does not reveal that theses fluorophores must be high-oxidation or low oxidation organic compounds. EEM is a holistic approach to characterize complex COM in the environment.

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- *Chen, Q., Hua, X., Dyussenova, A., et al.: Evolution of the chromophore aerosols and its driving factors in summertime Xi'an, Northwest China. Chemosphere 2021b, 281, 130838.*
- *Chen, Q., Miyazaki, Y., Kawamura, K., et al.: Characterization of chromophoric water-soluble organics in an urban, a forest, and the eastern equatorial Pacific aerosols using EEM and HR-ToF-AMS spectroscopy. Environ. Sci. Technol., 2016, 50, 10351-10360.*

Anonymous Referee #2 (accepted subject to minor revisions)

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 sufficiently for publication. I only have minor comments to improve the readability of the manuscript. My comments are outlined below.

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.

Minor Comments:

1. Line 11: Change 'result' to 'results'

We have revised "*result*" to "*results*" in line 12 in the improved paper.

2. Line 15-16: Change 'change the compositions' to 'changes the composition'

We have revised "*COM photodegradation not only change the compositions and properties*" to "*The combination of optical property, chemical component*" in line 14 in the improved paper.

3. Line 25: Change 'originate' to 'originates'

We have revised "*originate*" to "*originates*" in line 26 in the improved paper.

4. Line 29: Change 'process' to 'processing'

We have revised "*process*" to "*processing*" in line 31 in the improved paper.

5. Line 34-35: Change 'chromophores are photo-bleached' to 'chromophore photo-bleaching'

We have revised "*chromophores are photo-bleached*" to "*COM is photo-bleaching*" in line 37 in the improved paper.

6. Line 49: Remove 'ability on'

We have revised "*SOA may have a more significant ability on light absorption*" to "*SOA may have a more significant light absorption*" in line 48 in the improved paper.

7. Line 55: Change 'the complex photochemical reaction' to 'complex photochemical reactions'

We have revised "*Atmospheric COM could participate in the complex photochemical reaction, which further affect the aerosol aging*" to "*Photochemical process of COM largely determines the aerosol aging*" in line 54 in the improved paper.

8. Line 63-64: 'deactivate quickly with the ways of' to 'deactivates by'

We have revised "*^{1}COM* deactivate quickly with the ways of emitting photon (fluorescence) and intersystem crossing (triplet state, ^{3}COM*)*" to "*^{1}COM* deactivates by emitting photon (fluorescence) and intersystem crossing (triplet state (^{3}COM*) generation)*" in line 62-63 in the

improved paper.

9. Line 80: Change to 'in the laboratory'

We have revised "*in laboratory*" to "*in the laboratory*" in line 81 in the improved paper.

10. Line 132: Change 'Analysis error' to "Error analysis'

We have revised "*Analysis error*" to "*Error analysis*" in line 138 in the improved paper.

11. Line 182: Change 'opposite' to 'in contrast'

We have revised "*opposite*" to "*in contrast*" in line 192 in the improved paper.

12. Line 186: Change 'indicate' to 'indicates'

We have revised "*indicate*" to "*indicates*" in line 197 in the improved paper.

13. Line 187: Change 'opposite' to 'in contrast'

We have revised "*opposite*" to "*in contrast*" in line 198 in the improved paper.

14. Line 188-190: This sentence is unclear. Consider re-phrasing for clarity.

We have revised "*Organic matter with high molecular weight is photocomposed to small molecular weight and the molecular weight tend to be consistent following the photodegradation*" to "*The proportion of different molecular weight OM is nearly unchanged following the photodegradation in ambient PM*" in line 199-200 in the improved paper.

15. Line 217: Change 'consider' to 'considered'

We have revised "*consider*" to "*considered*" in line 228 in the improved paper.

16. Line 259: Change 'promote' to 'promotes'

We have revised "*promote*" to "*promotes*" in line 274 in the improved paper.

17. Line 296: Change 'lead' to 'leads'

We have revised "*lead*" to "*leads*" in line 315 in the improved paper.

18. Line 307-308: Change '…chemical compositions, and photochemical activity. The characteristics of COM photo-degradation were revealed.' to '…chemical composition, and photochemical activity to reveal the characteristics of COM photo-degradation.'

We have revised "*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*" to "*We made a comprehensive study in COM photodegradation and the effect of COM photodegradation on optical property, chemical component, and photochemical reactivity to reveal the characteristics of COM photodegradation*" in line 321-323 in the improved paper.

19. Line 320: Change 'dominant' to 'dominate'

We have revised "*dominant*" to "*dominate*" in line 334 in the improved paper.

20. Line 335: Change 'it' to 'this'

We have revised "*There were two reasons for it*" to "*There were two reasons for this*" in line 350 in the improved paper.

21. Line 339" Change 'would be" to 'could'

We have revised "*COM photodegradation would be play an important role in the content of ROS*" to "*COM photodegradation could play an important role in the content of ROS*" in line 354 in the improved paper.

22. Line 340: Change 'celebrate' to 'calibrate'. I believe this is the word that is intended.

We have revised "*celebrate*" to "*calibrate*" in line 355 in the improved paper.

23. Line 346: Change 'COM photodegradation have' to "COM photodegradation has a"

We have revised "*COM photodegradation have different impact on*" to "*COM photodegradation had a different impact on*" in line 361 in the improved paper.