

Thank you very much for the reviewer's suggestions for revision. According to the reviewer's suggestions, we have revised the paper. The reviewer's comments are in blue, the answers and revised text are in black.

Anonymous Referee #2

1. General comments

In this manuscript, the authors describe the formation of triplet state chromophoric dissolved organic matter (3CDOM) from a variety of aerosol samples, including laboratory generated primary organic aerosol and secondary organic aerosol, and ambient particulate matter, under simulated sunlight. Using trimethylphenol as a probe for 3CDOM*, all aerosol samples investigated formed 3CDOM* to a greater extent than the experimental control. The rate of formation of 3CDOM* in the aerosol samples was correlated with chemical and optical properties of the sample including fluorescence and UV-visible absorbance. The contribution of the 3CDOM* to form reactive oxygen species such as singlet molecular oxygen and hydroxyl radical was also quantified. The experiments described in this manuscript were thoughtfully designed and executed rigorously. However, the communication of these results should be improved before publication, as indicated in my comments below. The writing style used in this manuscript makes it challenging to read at times. For example, the authors often state a conclusion before giving context or discussing the data. This requires the reader to read through the paragraph more than once to be sure of the meaning. In addition, there are grammatical issues such as in the materials and methods section which switches between past and present tense. Better clarity in the writing would greatly improve this manuscript and better communicate these interesting results. Furthermore, some of the data was presented without sufficient discussion of its meaning and its larger scientific context. For example, discussion is lacking about why the correlation of AAE and kTMP differs between laboratory generated aerosol and ambient aerosol samples; why there is a lack of linear correlation between kTMP and contribution of CI for the SOA samples; and the meaning of the data shown in Figures 5 and 6.*

Thanks for the reviewer's suggestion. According to your opinion we have modified the paper. It will be helpful for improving this article. It mainly includes the following aspects.

1. A larger AAE value indicates a higher polarity of CDOM and degree of oxidation;

We have added “As shown in Figure 3, the AAE of POA and SOA are greater than Ambient PM, which indicate that CDOM of POA and SOA have a higher polarity” in the paper.

We have corrected “Figure 2” and “Figure 3”.

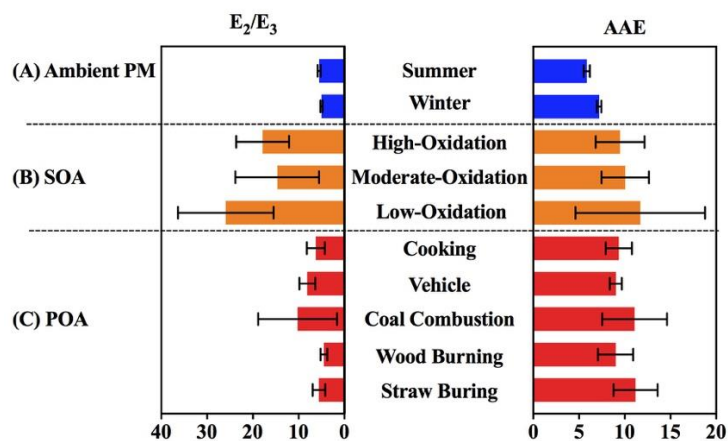


Figure 2. The characteristics of the AAE and E_2/E_3 ratio of different types of aerosols.

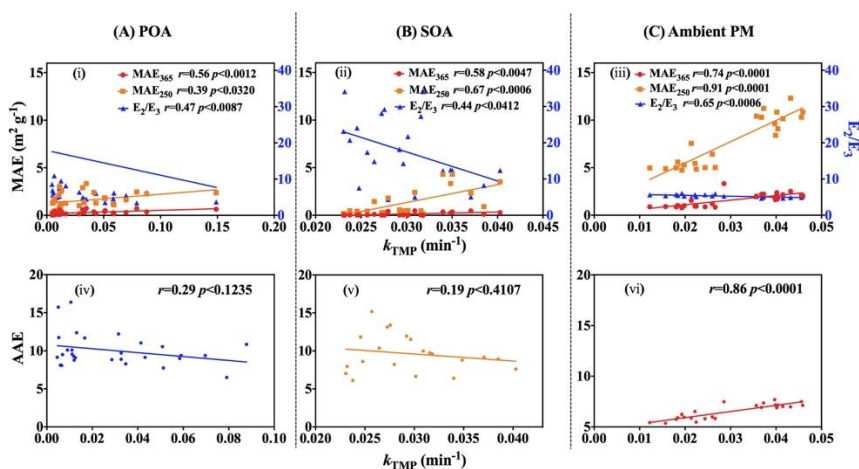


Figure 3. The characteristics of the correlation between k_{TMP} , the AAE, and the E_2/E_3 ratio. (i), (ii) and (iii) show the correlations between k_{TMP} , MAE and E_2/E_3 . (iv), (v) and (vi) show the correlations between k_{TMP} and the AAE. (A), (B) and (C) are POA, SOA and ambient PM sample results, respectively.

2. We have corrected the tense in Section;

For example, We have corrected “Triplet state formation experiments are carried out” to “Triplet state formation experiments were carried out”; We have

corrected “.....in the reactor are approximately 25 °C and 50%” to “.....in the reactor were approximately 25 °C and 50%”.

3. k_{TMP} does not varies with the content of C1 chromophore in SOA, so SOA is excluded from linear fitting.

For example, We have added “*In contrast, the proportion of the C1 component in SOA does not have a significant effect on the k_{TMP} , which illustrate that tryptophan do not have an effect on the formation rate of triplet state and CDOM driven by Maillard reaction may be the main substance that determines the rate of triplet state formation rate in SOA*” in the paper.

2. Specific comments:

1. Lines 10–13: It is not clear what the two types of identified CDOM were and how that relates to nitrogen-containing chromophores.

According to the comment we have corrected “*The structural-activity relationship between the CDOM type and the $^3\text{CDOM}^*$ formation capacity shows that the two types of $^3\text{CDOM}^*$ identified, which similar to the nitrogen-containing chromophores contributed 88% to the formation of $^3\text{CDOM}^*$* ” to “*The structural-activity relationship between the CDOM type and the $^3\text{CDOM}^*$ formation capacity shows that the CDOM tryptophan and the CDOM driven by the Maillard reaction, which similar to the nitrogen-containing chromophores, contributed 88% to the formation of $^3\text{CDOM}^*$* ” in the improved paper.

2. Line 50: The topic of the reference “You et al. 2012” does not match with the text.

We have deleted “ *$^3\text{CDOM}^*$ plays an important role in the oxidation of aniline- and sulfur-containing heterocyclic pollutants (You et al., 2012)*”.

3. Lines 78–80: This section of text is very repetitive and uses vague terms “types and compositions” multiple times. Please clarify what you mean by CDOM “types and compositions”.

We have corrected “*As a precursor of $^3\text{CDOM}^*$, CDOM has complex types and compositions. The types and abilities of CDOM to form $^3\text{CDOM}^*$ may be different, which requires us to analyze both the types and compositions of CDOM*” to “*CDOM as a precursor of $^3\text{CDOM}^*$, the abilities of the different types of CDOM to form*

³CDOM* may be different, which requires us to analyze both the chemical composition characteristics of the different types of CDOM”.

4. Lines 140–147: How long are the VOCs exposed to the low-oxidation and moderate oxidation conditions? The reaction time is only mentioned for the high-oxidation condition.

The reaction time of the LO, MO and HO are 6 h. We have corrected “The reaction time is not shorter than 6 h to ensure the complete reaction of VOCs” to “The reaction time of LO, MO and HO is not less than 6 h to ensure the complete reaction of VOCs”.

5. Lines 203–204: State what you used as the “high-concentration” and “low-concentration” for TMP.

The high-concentration of TMP is 400 μM and the low-concentration of TMP is 10 μM . We have added a state to the text, “we compared high-concentration TMP (400 μM) with low-concentration TMP (10 μM)”.

6. Lines 205–207: The reaction rate constant should not be expected to change with TMP concentration, but the rate of the reaction will change. The calculated k value on Figure S3 shows that the rate constant does remain essentially the same between the different concentration conditions.

This is due to the influence of the background sample at the low concentration of TMP. Compared with the reaction system of low concentration TMP, the difference of the consumption of high concentration TMP between aerosol samples and background are more significantly different.

We have corrected “the high-concentration TMP may have a relatively low background and a higher reaction rate constant” to “the high-concentration TMP may have a relatively low background and a higher reaction rate (The results are shown in Figure S3 of SI). Therefore, under the reaction condition of high concentration TMP, the aerosol sample is more significantly different from the background”.

7. Figure 1: Legend for A (ii) does not match terminology in figure caption of “LO, MO, and HO”. And the caption for graph C does not explain what data is presented.

We have corrected “*PO, MO and OO*” to “*LO, MO and HO*” in Figure.1. And we have corrected “*(C) The average consumption of TMP by aerosols does not conform to first-order kinetics*” to “*(C) The consumption characteristic of TMP by aerosols does not conform to first-order kinetics. SB is straw burning, V is vehicle exhaust*”.

8. Lines 305–307: The first two sentences of section 3.2 seem to be contradicting each other. It is stated that the $^3\text{CDOM}^$ formation rate is different for each aerosol source, but then the data is presented to show that the average formation rate is the same for all aerosol sources.*

We have corrected “*The $^3\text{CDOM}^*$ formation ability of different sources aerosols is different*” to “*The formation ability of $^3\text{CDOM}^*$ by different sources aerosols are compared*”.

9. Lines 312–314: The TMP rate constants should be state for both the straw and wood burning samples.

We have stated the reaction rate constants of straw and wood combustion.

We have corrected “*the k_{TMP} values of the straw burning samples are lower than those of the wood burning samples (0.035 min^{-1})*” to “*the k_{TMP} values of the straw burning samples (0.035 min^{-1}) are lower than those of the wood burning samples (0.048 min^{-1})*”.

10. Lines 314–316: Phenolic compounds would be expected to be present in both the wood burning samples and straw burning samples. How do you explain the difference in k_{TMP} for these two samples?

Phenols are not likely precursors to form triplet state. As shown in Figure 5, the contribution of C1 and C3 to triplet state formation is different, which caused difference of triplet state formation between wood burning and straw burning.

11. Lines 324–330: Its surprising to me that the $^3\text{CDOM}^$ does not depend strongly on the SOA precursor. Especially since these SOA materials will have different light absorbance properties. Do you have any further insight into why the $^3\text{CDOM}^*$ formation is so similar between these samples?*

We have mentioned “³CDOM* formation of C1 is promoted by the increase in the oxidation degree” and “C3 is oxidized and decomposed by the increase in the oxidation degree” in the paper. The contribution of C2 and C4 to fluorescence varies with the degree of oxidation. However, neither of these CDOM contributes significantly to the formation of triplet state. Therefore, we insist that the fluorescence characteristics of CDOM in SOA are related to the oxidation degree of the formation of SOA, but oxidation degree do not directly affect the formation of triplet states.

12. Lines 353–355: The strength of the correlations should be state in the text. In most cases there is only a moderate correlation between MAE or E2/E3 and kTMP.

We expect that the relationship between k_{TMP} and chemical characteristics can be studied by value. Although the correlation is moderate, aerosols from different sources basically show the same trend, which reflects the feasibility of this method.

13. Lines 369–372: Why would the correlation of kTMP and AAE be opposite between POA, SOA, and ambient PM? This result should be discussed further.

A larger AAE value indicates a higher polarity of CDOM and degree of oxidation. We expect to determine its ability to form triplet state based on the characteristics of the CDOM. We have added “the AAE of POA and SOA are greater than Ambient PM, which indicate that CDOM of POA and SOA have a higher polarity” in the paper.

14. Line 377: “The ³CDOM formation ability depends on the CDOM type.” The data to support this claim is not presented until the following paragraph and it does not fit the topic of the paragraph it is in.*

We have deleted “The ³CDOM* formation ability depends on the CDOM type” in the paper.

15. Line 382: The comparison of the excitation-emission peaks to tryptophan and products from the Maillard reaction should have a reference.

We have added the references in the text.

- Hawkins, L. N., Lemire, A. N., Galloway, M. M., Corrigan A, L., Turley, J. J., Espelien, B. M., De Haan, D. O. Maillard Chemistry in Clouds and Aqueous Aerosol As a Source of

Atmospheric Humic-Like Substances, Environ. Sci. Technol., 50, 7443-7452, <http://doi.org/10.1021/acs.est.6b00909>, 2016.

- De Haan, D. O., Hawkins, L. N., Kononenko, J. A., Turley, J. J., Corrigan, A. L., Tolbert, M. A., Jimenez, J. L. Formation of Nitrogen-Containing Oligomers by Methylglyoxal and Amines in Simulated Evaporating Cloud Droplets, Environ. Sci. Technol., 45, 984-991, <http://doi.org/10.1021/es102933x>, 2010.

16. Lines 383–384: The content of C3 in the samples is quite variable and seems to be a significant fraction in the moderate-oxidation and low-oxidation SOA samples. Could this tell you more about the SOA composition under different oxidation conditions?

We have discussed in paper as following.

“With increasing oxidation degree, the content of C3 decreases. The contribution of C3 to fluorescence 2.0%, 19.9% and 33.8%, which indicates that C3 is oxidized and decomposed (Wong et al., 2015). The contributions of C3 to ³CDOM are 66.4%, 33.2% and 4.8%, respectively”.*

17. Figures S7–S10 should be referenced directly in the main text.

Figure S7-S10 have been referenced in the text.

Line 390: *“5 types of CDOM were identified through the PARAFAC model (Model error comparisons shown in Figure S7 and S8 of SI)”.*

Line 409: *“The structure-activity relationship between the CDOM type and ³CDOM* formation rate was established by the improved PARAFAC model in equation (2) (Residual of model as shown in Figure S9 and S10 of SI)”.*

18. Lines 417–418: It would be helpful to refer back to the reaction pathways in Scheme 1 during this discussion.

We have corrected it in the improved paper.

We have corrected *“The quenching mechanism is mainly energy transfer, ^[1]_{SEP} which means that this ³CDOM* has more significant effect of driving ROS”* to *“The quenching mechanism is mainly energy transfer (as shown in (3) of Scheme 1), which means that this ³CDOM* has more significant effect of driving ROS”.*

19. Lines 420–422: The lack of correlation of CI in the SOA samples with k_{TMP} should be discussed as well.

We have added “*In contrast, the proportion of the CI component in SOA does not have a significant effect on the k_{TMP} , which illustrate that tryptophan do not have an effect on the formation rate of triplet state and CDOM driven by Maillard reaction may be the main substance that determines the rate of triplet state formation rate in SOA*” in the improved paper.

20. Line 430: It is not clear what is meant by “external mixing state of photochemical aging level”.

This statement indicates that atmospheric particles come from different sources, and the photochemical activity of particles from different sources is different. Each particle in the atmosphere may have a different photochemical activity due to different sources.

21. Lines 431–432: The relative contribution of $^3\text{CDOM}^$ to overall oxidation is not shown in Table S1. I could not find this data in the paper or the supporting information.*

The formation rate of $^3\text{CDOM}^*$ in the actual atmosphere are shown in last column of Table S1.

22. Lines 445–464: This section with the data on ROS production would be better suited in the Results & Discussion section of the paper.

Our experiments proved the driving effect of triplet state on active oxygen, and further proved the potential effect of triplet on aerosol aging. Moreover, we only conducted 2 experiments, respectively. The current experimental results are not systematic. We explained the environmental significance of studying the triplet state through this section.

23. Lines 446–450: The meaning of the signals and the type of sample shown in Figures 5 and 6 should be explained. As well, parts (a) and (b) should be explained in the text.

We have added “*As shown in (a) of Figure 5 and Figure 6, there are no obvious signals of $\bullet\text{OH}$ and $^1\text{O}_2$ without illumination*” in the improved paper.

Supporting information:

1. Table S3: categories of oxidation should match text in main paper, with “low, moderate, and high oxidation”.

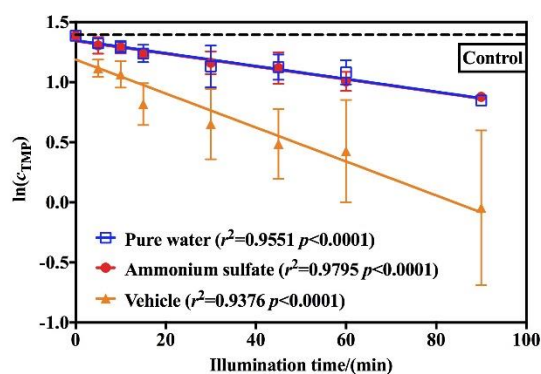
According to the comment we have corrected it in the improved paper.

2. Figure S3: The label for the concentration of TMP shows $4 \times 10^2 \mu\text{M}$, but this does not match with the main text description that the TMP concentration is 4 mM ($4 \times 10^3 \mu\text{M}$).

We have corrected “4 mM” to “ $4 \times 10^2 \mu\text{M}$ ”.

3. Figure S4: Legend has incorrect spelling of ‘ammonium’.

We have corrected it in Figure S4.



Technical corrections:

1. Line 1: “chromophore” -> “chromophoric”

We have corrected it in the improved paper.

2. Line 3: “driving” -> “drive”

We have corrected it in the improved paper.

3. Lines 6 – 8: The wording of this sentence is unclear: “Biomass combustion has the strongest 3CDOM^* generation capacity and the weakest vehicle emission capacity.”

Is this trying to say that vehicle emissions have the weakest 3CDOM^* generation?

We have corrected “Biomass combustion has the strongest 3CDOM^* generation capacity and the weakest vehicle emission capacity” to “Biomass combustion has the strongest 3CDOM^* generation capacity and vehicle emission capacity is the weakest”.

4. Line 11: *“structural-activity”* -> *“structure-activity”*

We have corrected it in the improved paper.

5. Line 85: *“expected”* -> *“well-suited”*

We have corrected it in the improved paper.

6. Line 128: *“is collected”* -> *“was collected”*

We have corrected it in the improved paper.

7. Line 266: *“were selected”* -> *“was selected”*

We have corrected it in the improved paper.

8. Line 420: *“Figure 3D”* -> *“Figure 4D”*

We have corrected it in the improved paper.

9. Line 428: *“has”* -> *“have”*

We have corrected it in the improved paper.

10. Line 646: *Incorrect spelling of author’s name: “Canonica”*

We have corrected it in the improved paper.