Response to reviewers for the manuscript "Photo-degradation of atmospheric chromophores: type conversion and changes in photochemical reactivity" (acp-2020-1223)

We appreciate the comments from the editor and 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.

Response to Anonymous Referee #1

The manuscript "Photo-degradation of atmospheric chromophores: type conversion and changes in photochemical reactivity" addressed the photochemical degradation of atmospheric COM and a loss of this material of 70% within 7 days of light exposure. The involvement of reactive oxygen species also was addressed. Grammar should be checked and grammatical errors are distracting in reading the manuscript. The presented data does not add a lot of additional information on the photochemical behavior of aerosols. Previous studies described in detail the photochemical kinetics on more relevant SOA. It is not clear to me what the novelty of this paper is and perhaps the authors need to strengthen and highlight better the novel contribution. It also was not helpful to see limited details in the method sections. More specifically, it is not clear to me how the aerosols generated here in the lab resembles similarity to once in the atmosphere. An explanation is needed why the combustion of wheat straw, corn straw, rice straw and wood was chosen to generate aerosols. To elaborate on my assessment, please see more specific comments below:

We appreciate the comments from reviewer. We appreciate the positive evaluation of this work. 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) We studied the characteristics of COM photo-degradation, the potential effects of COM photolysis on the photochemical reactivity, and the contribution of COM to reactive oxygen species (ROS) in aerosol in this paper. The novelty of this paper is the characteristics and mechanisms of COM photolysis and the effect of COM photolysis on aerosol aging. We have corrected the paper to strengthen and highlight better the novel contribution. For example,

We have corrected "*the characteristics of COM photo-degradation and the potential effects of COM photolysis on the photochemical reactivity are illustrated*" to "*Here, we report the characteristics of COM photo-degradation, the potential effects of COM photolysis on the photochemical reactivity, and the contribution of COM to reactive oxygen species (ROS)*" in abstract in the improved paper.

We have corrected "*In order to illustrate the effect of COM photo-degradation on the optical properties and photochemical reactivity in aerosols, we simulate the photolysis process of primary organic aerosol (POA) and ambient particle matter (ambient PM) in laboratory*" to "*The chemical composition and atmospheric quality are significantly affected by aerosol aging. In order to illustrate the properties of COM and the effect of COM photolysis on aerosol aging, we simulate the*

process of COM photolysis and COM inducing ROS in primary organic aerosol (POA) and ambient particulate matter (ambient PM) in laboratory" in section 1 in the improved paper.

We have added "*We made a comprehensive study of COM photo-degradation, changes in optical properties and chemical compositions, the effect of COM photo-degradation on photochemical activity and aerosol aging. The properties of COM photo-degradation were revealed. COM photo-degradation could be explained by reduction of carbonaceous components, decrease of light absorption capacity, and attenuation of fluorescence intensity. There are great differences in various COM in aerosols. Therefore, we suggested that the properties COM photo-degradation could be comprehensively characterized by carbonaceous components and optical characteristics*" in section 4 in the improved paper.

We have added "*The effects of COM photo-degradation on the photochemical activity in aerosols are studied. We evaluated the effect of COM photo-degradation on the photochemical activity. The ability of triplet state generation and $^1O_2$ yield was chosen to quantify the photochemical activity*" in section 4 in the improved paper.

(2) We described the generated method of POA in detail. The supplementary and revision of method have been added in the improved paper. For example,
We added the schematic of combustion equipment in improved paper.

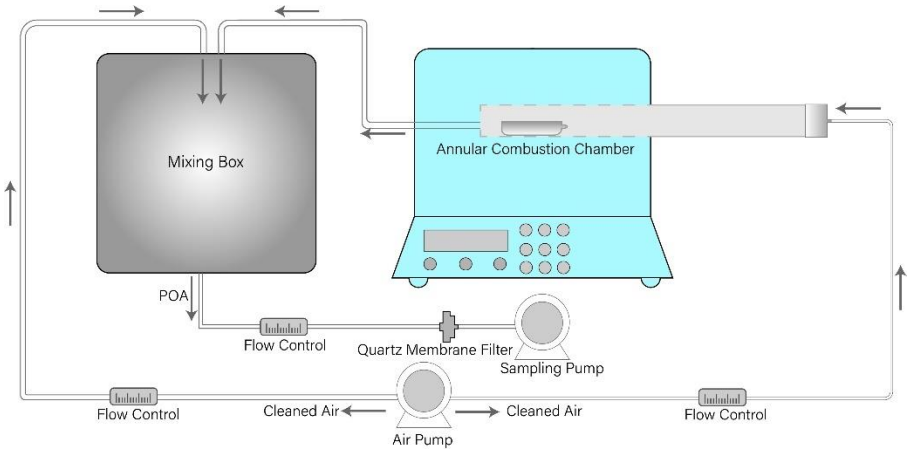


Fig.1 Schematic diagrams of combustion equipment for POA.

We have corrected "*Wheat straw, corn straw, rice straw and wood were burned at about 500 ℃ in the tube stove*" to "*As shown in Fig.1, Wheat straw, corn straw, rice straw and wood were burned in the annular combustion chamber when temperatures rose to 500 ℃*" in section 2.1 in the improved paper.

We have corrected "*A high-purity quartz reactor was designed for the photolysis experiment (Fig.1a). A rubber gasket was embedded on the upper edge of the reactor. The reactor was clamped with a high-purity quartz cover to form a sealed environment*" to "*The material of reactor is quartz (Fig.2a) and the reactor was designed for photolysis experiment. The reactor was sealed through clamping a quartz cover to reactor*" in section 2.2 in the improved paper.

We have corrected "*Two vents were designed in the low position of the reactor. The vents were connected to water circulator to ensure that the temperature was about 25°C in the reactor*" to "*Two*

air vents were used to air exchange and Two water cycle vents were connected to water circulator to ensure that the temperature was about 25°C in the reactor" in section 2.2 in the improved paper.

(3) Straw and coal burning are the main way of heating in China, especially in the rural areas. Coal burning is also the main source of energy in China. Therefore, the combustion of wheat straw, corn straw, rice straw and wood were chosen to generate aerosols.

We have added "*Straw and coal burning are the main way of heating and cooking in the rural areas in China. Therefore, the combustion of wheat straw, corn straw, rice straw and wood were chosen to generate aerosols*" in section 2.1 in the improved paper.

1. Actinometry needs to be undertaken to confirm the dose of light in the reaction chamber, otherwise it is not clear what the exposure was according to the geometry and pathlength.

(1) The light intensity was measured by an optical radiometer (Perfectlight Inc.) and the absorbance can be estimated in the reactor (Fig.2). Each sample was placed in the same position under the same light intensity to maintain the same dose of light.

(2) According to the previous study (Laszakovits et al., 2017), we calculated the dose of light by chemical method.

We have added "*4-nitroanisole (PNA, 10 μM) and pyridine (pyr, 10 mM) were used in the method. Firstly, the absorbance of the mixture of 4-nitroanisole and pyridine was measured. Then, the mixture of 4-nitroanisole and pyridine was photolyzed in the reactor (Fig.2). The concentration of pyridine was measured by HPLC and the decay dynamics was calculated.*

$$I_\lambda = \frac{k'[PNA]_0 l}{1000\Phi(1-10^{-\varepsilon_\lambda l[PNA]_0})} \quad (4)$$

$$\Phi = 0.29[pyr] + 0.00029 \quad (5)$$

in equation (4) and (5),

k'-First order reaction rate constant of pyr (s^{-1});

$[PNA]_0$-Initial molar concentration of pyr;

ε_λ- molar absorbance index of PNA at the wavelength of λ ($M^{-1} \cdot cm^{-1}$);

l-Optical path (1 cm);

Φ-Quantum yield of PNA (mol • $einstein^{-1}$)." in Text S2 in the improved paper.

- *Laszakovits, J.R., Berg, S.M., Anderson, B.G., O'Brien, J.E., Wammer, K.H., Sharpless, C.M.: p-Nitroanisole/Pyridine and p-Nitroacetophenone/Pyridine Actinometers Revisited: Quantum Yield in Comparison to Ferrioxalate, Environ. Sci. Tech. Let., 4, 11-14, http://dx.doi.org/10.1021/acs.estlett.6b00422, 2017.*

2. Line 128: what was the dilution factor?

The dilution factor is the dilution ratio of extracts and the specific dilution factor has been added in Table S2.

Table S2. *OC concentration of samples for optical analysis.*

POA				Ambient PM			
Sample ID	**c_{WSOC}/ppm**	**c_{WISOC}/ppm**	**Dilution factor (WSOC/WISOC)**	**Sample ID**	**c_{WSOC}/ppm**	**c_{WISOC}/ppm**	**Dilution factor (WSOC/WISOC)**
1-0h	2.99	6.86	40/40	9-0h	59.12	7.42	1/5
1-2h	2.91	2.87	40/40	9-2h	65.85	5.48	1/5
1-6h	3.13	2.52	40/40	9-6h	67.39	8.30	1/5
1-12h	3.51	2.67	40/40	9-12h	55.90	6.36	1/5
1-24h	3.76	2.68	40/40	9-24h	54.41	7.20	1/5
1-3d	3.02	2.15	40/40	9-3d	76.46	4.41	1/1
1-7d	3.00	2.24	40/40	9-7d	63.24	2.95	1/1
2-0h	3.60	2.96	40/40	10-0h	52.97	3.52	1/5
2-2h	4.19	2.85	40/40	10-2h	54.92	7.25	1/5
2-6h	4.00	3.22	40/40	10-6h	61.99	7.12	1/5
2-12h	3.60	0.73	40/40	10-12h	53.09	4.94	1/5
2-24h	4.13	3.78	40/40	10-24h	48.29	4.68	1/5
2-3d	3.38	4.46	40/40	10-3d	48.15	4.01	1/1
2-7d	3.31	2.64	40/40	10-7d	53.70	3.82	1/1
3-0h	5.86	3.15	40/60	11-0h	6.62	2.79	10/10
3-2h	6.13	3.31	40/60	11-2h	4.99	4.61	10/10
3-6h	6.31	5.26	40/40	11-6h	4.10	4.22	10/10
3-12h	6.20	2.51	40/40	11-12h	5.01	1.67	10/10
3-24h	5.19	5.44	40/40	11-24h	5.59	2.84	10/10
3-3d	5.02	4.09	40/40	11-3d	3.66	0.47	1/10
3-7d	4.70	4.90	40/40	11-7d	5.34	1.08	1/10
4-0h	4.22	2.40	40/40	12-0h	5.65	3.62	10/10
4-2h	4.40	2.90	40/40	12-2h	3.75	3.81	10/10
4-6h	4.02	2.90	40/40	12-6h	7.15	4.38	10/10
4-12h	3.15	5.38	40/40	12-12h	4.98	3.17	10/10
4-24h	3.94	2.62	40/40	12-24h	4.54	2.92	10/10
4-3d	3.22	2.98	40/40	12-3d	4.03	1.42	1/1
4-7d	3.29	2.30	40/40	12-7d	5.84	1.45	10/10
5-0h	5.02	2.24	40/60	13-0h	59.68	2.90	1/5
5-2h	4.74	3.82	40/40	13-2h	57.95	3.71	1/5
5-6h	5.26	4.02	40/40	13-6h	50.79	5.19	1/5
5-12h	5.46	3.94	40/40	13-12h	52.57	3.24	1/5
5-24h	5.21	4.13	40/40	13-24h	54.15	1.34	1/5
5-3d	4.72	4.85	40/40	13-3d	55.65	1.85	1/5
5-7d	3.67	3.53	40/40	13-7d	55.99	1.74	1/1
6-0h	5.23	2.46	40/60	14-0h	58.12	1.86	1/5
6-2h	5.52	2.58	40/60	14-2h	47.04	4.06	1/5
6-6h	4.49	4.50	40/40	14-6h	48.95	2.13	1/5
6-12h	4.28	3.72	40/40	14-12h	49.47	2.80	1/5
6-24h	4.23	3.76	40/40	14-24h	39.93	3.70	1/5
6-3d	4.01	4.14	40/40	14-3d	29.66	0.63	1/1
6-7d	3.64	3.42	40/40	14-7d	49.12	0.59	1/1
7-0h	9.66	3.59	40/80	15-0h	42.22	2.67	1/40
7-2h	6.75	3.88	40/80	15-2h	32.35	---	1/40
7-6h	8.24	4.23	40/80	15-6h	26.49	4.96	1/40

Table S2 (continued)

POA				Ambient PM			
Sample ID	**c_{WSOC}/ppm**	**c_{WISOC}/ppm**	**Dilution factor (WSOC/WISOC)**	**Sample ID**	**c_{WSOC}/ppm**	**c_{WISOC}/ppm**	**Dilution factor (WSOC/WISOC)**
7-12h	9.33	4.26	40/80	15-12h	32.87	1.62	1/40
7-24h	7.62	4.06	40/80	15-24h	26.60	2.60	1/40
7-3d	7.23	3.70	40/80	15-3d	26.04	---	1/1
7-7d	6.37	5.21	40/80	15-7d	33.67	3.06	1/1
8-0h	9.43	4.02	40/80	16-0h	38.66	0.93	1/10
8-2h	9.34	2.24	40/160	162h	27.01	3.07	1/10
8-6h	9.34	4.47	40/80	16-6h	29.22	2.56	1/20
8-12h	9.13	4.30	40/80	16-12h	31.84	1.24	1/10
8-24h	8.51	4.41	40/80	16-24h	44.70	1.19	1/10
8-3d	6.90	5.54	40/80	16-3d	27.32	0.27	1/1
8-7d	7.09	4.83	40/80	16-7d	50.43	1.05	1/1

3. Line 134: How many samples were used to create the model? Were water soluble and methanolic samples combined in the dataset to create the PARAFC model? How were the EEMs of the methanolic extract measured?

111 samples were used to create the model. In order to compare the change characteristics of water-soluble and water-insoluble chromophores during photolysis, water soluble and methanolic samples combined in the dataset to create the PARAFC model. The methanol background was analyzed and the background was subtracted. The analytical method of methanolic extract is "*The absorption spectra were recorded in the wavelength range of 200-600 nm. The range of excitation wavelength was 200-600 nm and the range of excitation wavelength was 250-800 nm. The interval was 5 nm. The exposure time was 0.5 s*" in section 2.5.

We have added "*111 samples were used to create the model. WSOM and WISOM were combined in the dataset to create the PARAFC model*" in section 2.5 in the improved paper.

We have corrected "*The background samples were also analyzed using the same method and the background signals were subtracted from the sample signals*" to "*Water and methanol background samples were analyzed using the same method and the background signals were subtracted from the sample signals*" in section 2.5 in the improved paper.

4. Line 150: Was is isocratic and at what retention time did TMP elute?

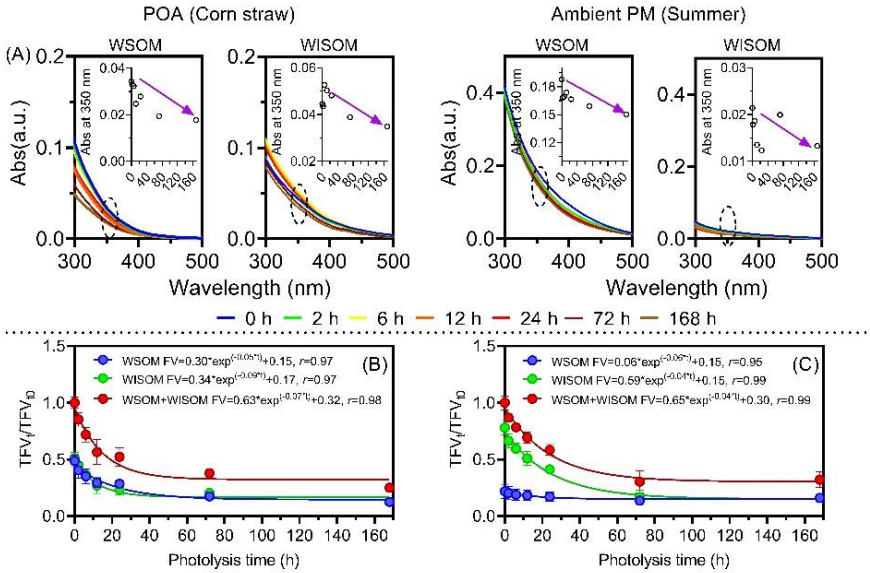
Based on previous studies (Canonica et al., 2000; Kaur & Anastasio, 2018), we optimized the previously reported method. The elution process is isocratic. The retention time is 14.5 min.

We have added "*The retention time is 14.5 min*" in section 2.6 in the improved paper.

- Canonica, S., Hellrung, B., Wirz, J.: Oxidation of Phenols by Triplet Aromatic Ketones in Aqueous Solution, J. Phys. Chem. A, 104, 1226-1232, http://dx.doi.org/10.1021/jp9930550, 2000.
- Kaur, R., Anastasio, C.: First Measurements of Organic Triplet Excited States in Atmospheric Waters. Environ. Sci. Tech., 52, 5218-5226, http://dx.doi.org/10.1021/acs.est.7b06699, 2018.

5. Figure 3: The raw absorbance should be converted to apparent absorption coefficient a, so that it is normalized to pathlength.

Fluorescence spectra of COM was measured, but we could not obtain the molecular composition. Therefore, it is difficult to obtain the apparent absorption coefficient. However, the absorbance has been normalized. We have corrected the **Fig.3** in improved paper.



6. Line 220: It is very easy to contaminate fluorescence samples that than show protein like fluorophores. How did the blank samples compare? Was this protein-like fluorescence apparent in controls? This needs to be carefully addressed so that QA/QC can be assessed.

As shown in the Fig.R1, the first figure is the background. The second figure is the extract of POA. The background contributes essentially nothing to the fluorescence intensity of sample at the peaks of Ex./Em. = 230/300 nm. Therefore, the experimental results are reliable.

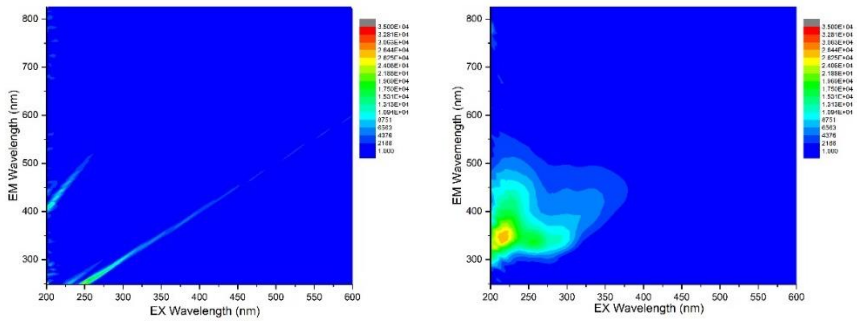


Fig. R1. Comparison of the EEMs of background and sample. The first figure is the background. The second figure is the extract of POA.

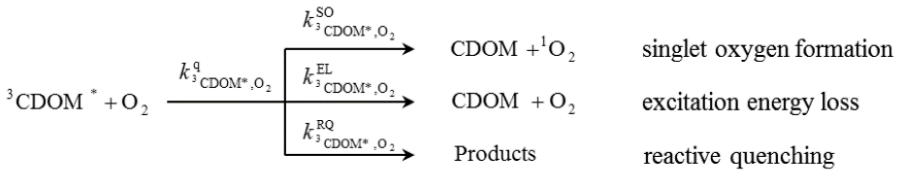
7. Line 240: Triplet state of what?

We have corrected "*The photochemical activity is characterized by triplet state and singlet oxygen*" to "*The photochemical activity is characterized by the generating ability of ^{3}COM* and singlet oxygen*" in section 3.3 in improved paper.

8. Line 270-280: It is well known that singlet oxygen is photochemically generated and very well correlated to UV-vis absorption, so this all seems to me a generic trend that has been described low-energy 3COM even exists and less so being the main precursor of singlet oxygen, but of course this is debatable.*

As mentioned by the reviewer, singlet oxygen is photochemically generated. Previous study has suggested the ^{3}COM* induce $^1O_2$ significantly (Schematic R1).

We obtained the mechanism and characteristic of ^{3}COM* inducing $^1O_2$ by the method of combining capturing agent and EPR. There are obviously different of $^1O_2$ in the POA and ambient PM after ^{3}COM* was quenched by sorbic acid. Therefore, we propose that the generating ability of $^1O_2$ was affected by ^{3}COM* energy in POA and ambient PM.



Schematic R1. Deactivation Pathways for ^{3}COM* in the Presence of Oxygen (Rosario-Ortiz et al., 2016)

- Rosario-Ortiz, F. L., and Canonica, S.: Probe Compounds to Assess the Photochemical Activity of Dissolved Organic Matter, Environ. Sci. Technol., 50, 12532-12547, http://dx.doi.org/10.1021/acs.est.6b02776, 2016.

Response to Anonymous Referee #2

The manuscript 'Photodegradation of atmospheric chromophores: type conversion and changes in photochemical reactivity' provides results on the photochemical aging of atmospheric aerosols. The results include OC/EC analysis, parallel factor (PARAFAC) analysis of excitation-emission matrices, and photosensitization of singlet oxygen with each measured as a function of solar irradiation. The results are of interest and merit eventual publication in the atmospheric chemistry literature, however, the novelty, writing, and presentation require significant improvement and does not meet the standard for publication in Atmospheric Chemistry and Physics in its current state. My comments are outlined below.

We appreciate the comments from reviewer. We appreciate the positive evaluation of this work. 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.

General comment: The manuscript would benefit greatly from a substantial revision to improve the writing quality (see minor comments for extensive recommended changes), conceptual framework, and referenced literature, to increase the readability of this work.

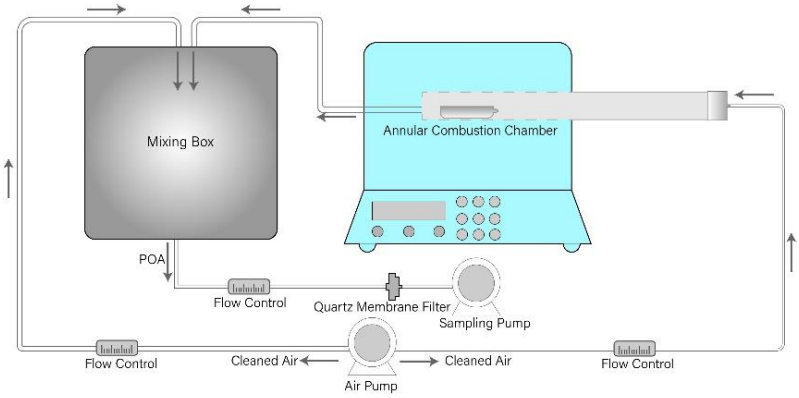
In order to increase the readability of this paper, we have revised the description of the experimental method, the structure of sentences, and the Figures in this paper. We have improved our writing. For example,

We have corrected "*A high-purity quartz reactor was designed for the photolysis experiment (Fig.1a). A rubber gasket was embedded on the upper edge of the reactor. The reactor was clamped with a high-purity quartz cover to form a sealed environment. Two vents were designed in the low position of the reactor. The vents were connected to water circulator to ensure that the temperature was about 25°C in the reactor*" to "*The material of reactor is quartz (Fig.2a) and the reactor was designed for photolysis experiment. The reactor was sealed through clamping a quartz cover to reactor. Two air vents were used to air exchange and Two water cycle vents were connected to water circulator to ensure that the temperature was about 25°C in the reactor*" in section 2.2 in the improved paper.

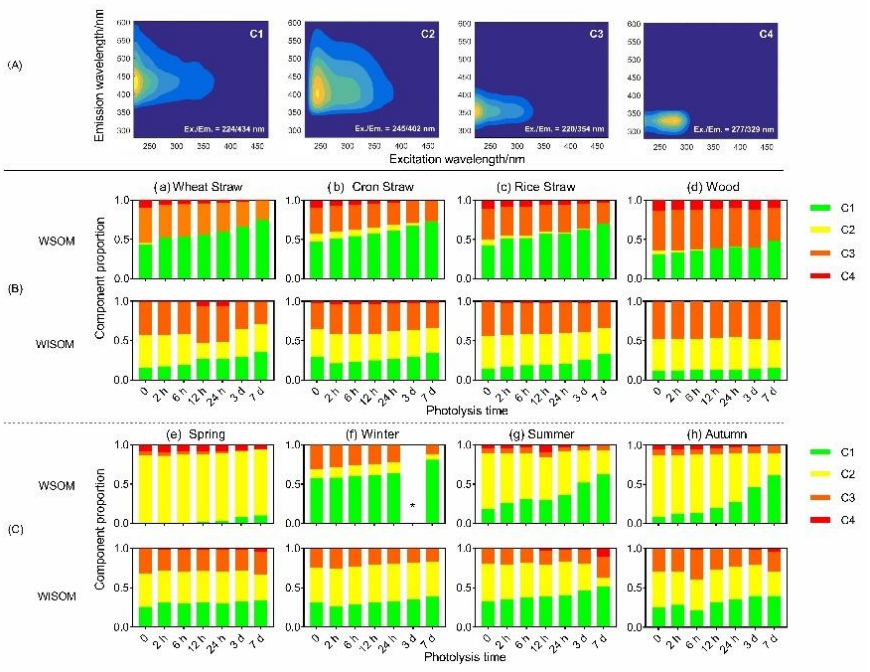
We have corrected "*Wheat straw, corn straw, rice straw and wood were burned at about 500 ℃ in the tube stove*" to "*As shown in Fig.1, Wheat straw, corn straw, rice straw and wood were burned in the annular combustion chamber when temperatures rose to 500 ℃*" in section 2.1 in the improved paper.

We have corrected "*The low attenuation result from COM have undergone a long-term atmospheric aging process and the water-soluble COM are easier to photolysis*" to "*The results suggest that COM have undergone a long-term atmospheric aging and water-soluble COM have greater ability to be photolyzed*" in section 3.2 in the improved paper.

We have added the Fig.1 in the improved paper.



We have corrected the Fig.5 in the improved paper.



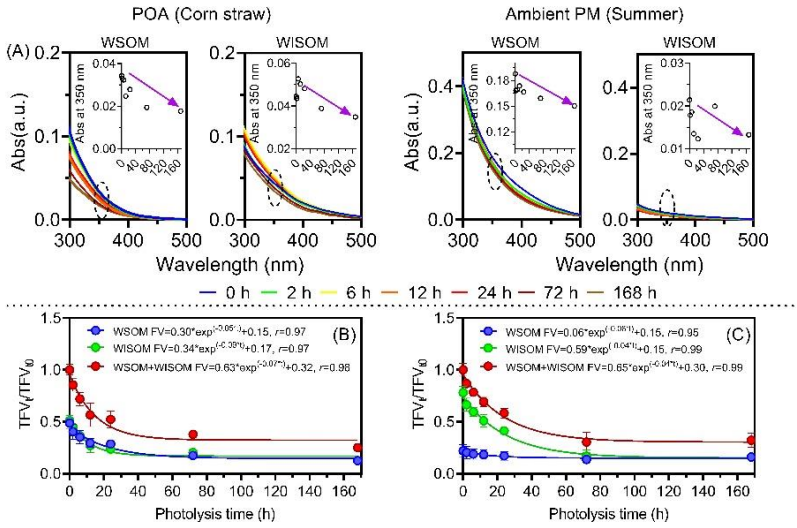
Major comments: 1) The title of this manuscript could be revised to remove the 'type conversion' terminology which is ambiguous and not commonly used. I would recommend making it more explicit that you are talking about oxidation by revising to: Photodegradation of Atmospheric Chromophores: Changes in Oxidation State and Photochemical Reactivity.

We have corrected "*Photo-degradation of atmospheric chromophores: type conversion and changes in photochemical reactivity*" to "*Photodegradation of Atmospheric Chromophores: Changes in Oxidation State and Photochemical Reactivity*".

2) In the first paragraph of section 3.2, the results on the decrease in absorbance vs. fluorescence (or TFV) are not well separated and it is extremely difficult to separate when the authors are referring to absorbance or the fluorescence of these. It appears decay constants are provided for TFV but nor for absorbance. . .. Do the photolysis decay kinetics differ significantly for the chromophores vs. fluorophores? Or does the absorbance decay at the same rate as TFV?

We have corrected Fig.3. The decay of absorbance is different from TFV. We added the figure and data of absorbance at 365 nm to separate the attenuation characteristics of absorbance.

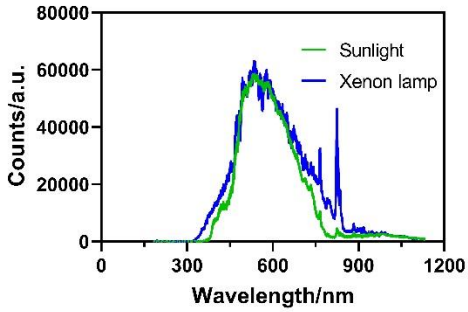
We have added "*As shown in the scatter plot (**Fig.4**), absorbance decreases significantly during photolysis. The decay kinetics of absorbance is different to fluorophores. The attenuation trend is inconstant, so the decay kinetics do not be mathematical analyzed and the absorbance also could confirm the photo-degradation of COM*" in section 3.2 in the improved paper.



3) What are the estimated atmospheric photolysis lifetimes including the factor of 1.2- 1.3 mentioned in Sec. 2.2? Also according to Figure S1 in the supplement, your light source has almost no flux

from 300-350 nm where the aerosols sample absorb most strongly and differs substantially from the solar spectrum. This should be addressed at some point in the manuscript.

The light intensity is various in different areas. The light intensity used in the experiment is approximately equal to the intensity in Xi'an and the actual lifetime can be estimated by multiplying 1.2-1.3. A more accurate assessment should be made in the actual atmospheric environment. We have corrected the Figure S1 in the improved paper.



4) On pages 8-9, the impacts of photolysis on the EEMs and individual components could be discussed in much more detail with comparison to more literature. Here are some additional references on this topic:

These references are very valuable to our study. Compared with previous study (Murphy et al., 2018), the results suggest that the number or shape of fluorophores do not change during COM photolysis in this paper.

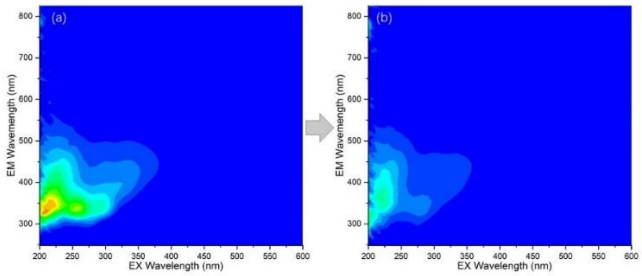


Fig.R2 Fluorescence spectra of POA before and after photolysis. (a) COM before photolysis. (b) COM after photolysis.

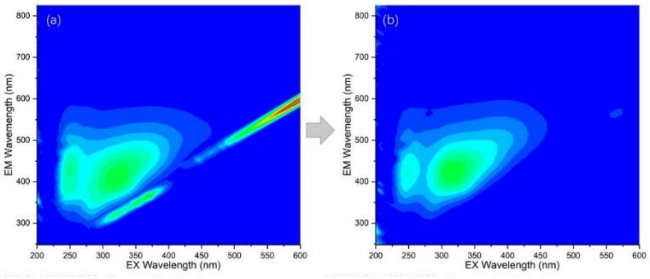


Fig.R3 Fluorescence spectra of Ambient PM before and after photolysis. (a) COM before photolysis. (b) COM after photolysis.

We have added "*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 (Murphy et al., 2018)*" in section 3.2 and "*COM could also be generated after light exposure (Harrison et al., 2020)*" in section 1 in improved paper.

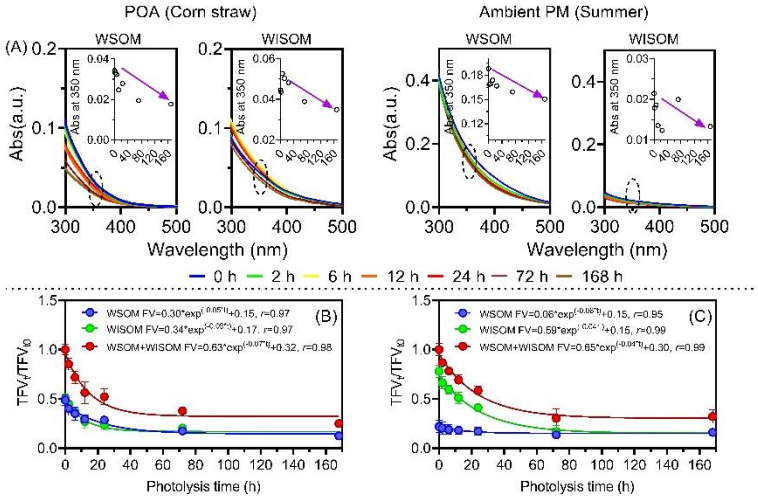
- *Murphy, K. R.; Timko, S. A.; Gonsior, M.; Powers, L. C.; Wünsch, U. J.; Stedmon, C. A. Photochemistry Illuminates Ubiquitous Organic Matter Fluorescence Spectra. Environ. Sci. Technol. 2018, 52 (19), 11243–11250*
- *Harrison, A. W.; Waterson, A. M.; De Bruyn, W. J. Spectroscopic and Photochemical Properties of Secondary Brown Carbon from Aqueous Reactions of Methylglyoxal. ACS Earth Space Chem. 2020, 4 (5), 762–773.*

5) In Figure 3A, the absorbances of WSOM and WISOM are nearly identical in the POA samples but differ by a factor of 10 in ambient PM. Is this a genuine difference in optical properties of these fractions i.e. does the water-soluble fraction actually absorb much more strongly than the water-insoluble fraction? This would be in contrast to previous brown carbon literature worth discussing in the manuscript. The use of mass absorption efficiency (MAE) is mentioned in the Supplement but not in the manuscript.

We have corrected Figure 3.

POA samples were generated in laboratory but the ambient PM was collected in actual atmosphere. The ambient PM has undergone a long-term aging. Therefore, light-absorbing substance in WISOM could be photolyzed and transformed so that WISOM has lower absorbances.

As shown in the scatter plot, absorbance decreases significantly during photolysis process, but the attenuation trend is inconstant. Therefore, MAE could be reference index but could not be mention the COM photo-degradation directly.



290 *6) Are the WSOM and WISOM combined for the PARAFAC analysis? I would expect that there would be some differences in the fluorophores present in each fraction. See this recent ACP paper where there are clear differences in the water-soluble and methanol-soluble fractions:*

In order to illustrate the difference of chromophores, 111 water-soluble and water-insoluble samples were used to create the PARAFAC model. Chen's study (Chen et al., 2020) has illustrated the
295 distribution characteristics of fluorophores in WSOM/WISOM. Tang's study (Tang et al., 2020) has been read and referenced in the improved paper.

We have added "*Tang et al. (2020) study the chromophores in water-soluble and water-insoluble samples, respectively. However, based on the Chen's study (2020), water-soluble and water-insoluble samples were combined to create the PARAFAC model so that illustrate the distribution*
300 *of chromophores in WSOM and WISOM*" in section 3.2 in the improved paper.

We have added "*111 samples were used to create the model. WSOM and WISOM were combined in the dataset to create the PARAFC model*" in section 2.5 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
305 sources of atmospheric chromophores by fluorescence excitation-emission matrix with parallel factor analysis, Sci. Total Environ., 718, 10, http://dx.doi.org/10.1016/j.scitotenv.2020.137322, 2020.
- Tang, J., Li, J., Su, T., Han, Y., Mo, Y.Z., Jiang, H.X., Cui, M., Jiang, B., Chen, Y.J., Tang, J.H., Song, J.Z., Peng, P.A., Zhang, G.: Molecular compositions and optical properties of

dissolved brown carbon in biomass burning, coal combustion, and vehicle emission aerosols illuminated by excitation-emission matrix spectroscopy and Fourier transform ion cyclotron resonance mass spectrometry analysis. Atmos. Chem. Phys. 20, 2513-2532, http://dx.doi.org/10.5194/acp-20-2513-2020, 2020.

7) Tabulation of the relative changes in each of the components in Figure 4B-C would improve the presentation of the results. This is information is all packed into the paragraph starting at Line 222 and is difficult to parse.

We have added the Table S4 and S5 in the SI.

Table S4. *Proportion of COM in POA.*

		WSOM				WISOM			
		C1	**C2**	**C3**	**C4**	**C1**	**C2**	**C3**	**C4**
Wheat Straw	0 h	0.44	0.02	0.45	0.10	0.15	0.42	0.42	0.01
	2 h	0.52	0.00	0.42	0.06	0.17	0.40	0.41	0.02
	6 h	0.54	0.00	0.41	0.05	0.19	0.39	0.40	0.02
	12 h	0.56	0.00	0.40	0.04	0.27	0.20	0.47	0.07
	24 h	0.60	0.00	0.37	0.03	0.27	0.21	0.46	0.06
	3 d	0.67	0.00	0.31	0.02	0.29	0.35	0.34	0.02
	7 d	0.75	0.01	0.24	0.01	0.36	0.35	0.28	0.02
Corn Straw	0 h	0.47	0.11	0.33	0.10	0.30	0.35	0.33	0.03
	2 h	0.51	0.10	0.32	0.07	0.21	0.37	0.38	0.03
	6 h	0.54	0.08	0.32	0.06	0.23	0.35	0.38	0.04
	12 h	0.57	0.08	0.30	0.05	0.25	0.34	0.38	0.04
	24 h	0.62	0.07	0.28	0.03	0.26	0.36	0.35	0.03
	3 d	0.68	0.03	0.28	0.01	0.30	0.34	0.34	0.03
	7 d	0.72	0.01	0.26	0.01	0.35	0.32	0.31	0.02
Rice Straw	0 h	0.42	0.08	0.39	0.11	0.15	0.42	0.42	0.02
	2 h	0.52	0.03	0.38	0.08	0.16	0.41	0.41	0.02
	6 h	0.52	0.03	0.37	0.08	0.19	0.40	0.40	0.02
	12 h	0.57	0.03	0.34	0.06	0.19	0.40	0.39	0.02
	24 h	0.57	0.02	0.35	0.06	0.20	0.39	0.39	0.02
	3 d	0.63	0.00	0.32	0.04	0.26	0.35	0.37	0.02
	7 d	0.70	0.00	0.26	0.03	0.33	0.33	0.32	0.01
Wood	0 h	0.30	0.06	0.51	0.13	0.12	0.40	0.48	0.01
	2 h	0.34	0.02	0.53	0.12	0.12	0.41	0.47	0.00
	6 h	0.36	0.01	0.51	0.12	0.13	0.40	0.47	0.00
	12 h	0.39	0.00	0.50	0.11	0.13	0.40	0.46	0.00
	24 h	0.40	0.01	0.49	0.10	0.13	0.42	0.46	0.00
	3 d	0.40	0.00	0.48	0.12	0.15	0.37	0.47	0.01
	7 d	0.49	0.00	0.41	0.10	0.15	0.36	0.48	0.00

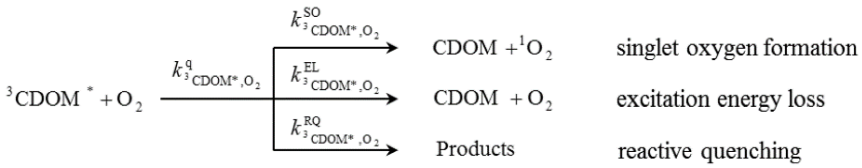
Table S5. *Proportion of COM in Ambient PM.*

		WSOM				WISOM			
		C1	**C2**	**C3**	**C4**	**C1**	**C2**	**C3**	**C4**
Wheat Straw	0 h	0.01	0.86	0.05	0.08	0.26	0.42	0.32	0.00
	2 h	0.00	0.86	0.05	0.09	0.31	0.40	0.27	0.01
	6 h	0.00	0.88	0.04	0.09	0.30	0.41	0.28	0.01
	12 h	0.01	0.87	0.03	0.08	0.31	0.40	0.27	0.01
	24 h	0.03	0.86	0.03	0.08	0.30	0.41	0.28	0.01
	3 d	0.08	0.83	0.02	0.07	0.33	0.39	0.26	0.02
	7 d	0.10	0.84	0.00	0.06	0.34	0.33	0.29	0.04
Corn Straw	0 h	0.34	0.49	0.15	0.02	0.31	0.44	0.24	0.01
	2 h	0.59	0.11	0.30	0.00	0.26	0.48	0.26	0.00
	6 h	0.59	0.14	0.27	0.00	0.29	0.47	0.24	0.00
	12 h	0.61	0.14	0.25	0.00	0.31	0.47	0.21	0.00
	24 h	0.63	0.14	0.23	0.00	0.33	0.48	0.19	0.00
	3 d	0.36	0.51	0.11	0.02	0.36	0.47	0.17	0.01
	7 d	0.08	0.89	0.00	0.04	0.39	0.44	0.16	0.01
Rice Straw	0 h	0.19	0.71	0.06	0.04	0.32	0.48	0.20	0.00
	2 h	0.26	0.63	0.07	0.04	0.35	0.44	0.20	0.01
	6 h	0.31	0.59	0.07	0.03	0.37	0.44	0.18	0.01
	12 h	0.30	0.55	0.06	0.09	0.39	0.40	0.19	0.03
	24 h	0.37	0.56	0.05	0.03	0.41	0.42	0.16	0.01
	3 d	0.52	0.41	0.06	0.01	0.46	0.34	0.18	0.02
	7 d	0.63	0.31	0.06	0.01	0.51	0.11	0.27	0.11
Wood	0 h	0.08	0.80	0.07	0.06	0.25	0.46	0.30	0.00
	2 h	0.12	0.74	0.08	0.06	0.28	0.42	0.29	0.01
	6 h	0.13	0.74	0.07	0.06	0.21	0.40	0.38	0.02
	12 h	0.20	0.68	0.07	0.04	0.32	0.41	0.26	0.01
	24 h	0.27	0.62	0.07	0.03	0.35	0.42	0.23	0.00
	3 d	0.46	0.44	0.09	0.02	0.40	0.39	0.20	0.01
	7 d	0.62	0.27	0.11	0.00	0.40	0.32	0.25	0.04

325

8) The paper demonstrates that low energy triplets are the main precursor for singlet oxygen , but do very high energy triplets form singlet oxygen with less efficiency in general? It would seem intuitive to me that when the energy gap between singlet and triplet COM is large, the photosensitization reaction will be less efficient.

As stated earlier, singlet oxygen is photochemically generated. Previous study has suggested the ^{3}COM* induce $^1O_2$ significantly (Schematic R1). We studied the mechanism and characteristic of ^{3}COM* inducing $^1O_2$ by the method of combining capturing agent and EPR. There are obviously different in $^1O_2$ in the POA and ambient PM after ^{3}COM* was quenched by sorbic acid. In POA, high energy ^{3}COM* was quenched and the $^1O_2$ still exist. However, high energy ^{3}COM* was quenched but the $^1O_2$ disappears in ambient PM. Therefore, we illustrated that low energy ^{3}COM* are the main precursor for singlet oxygen. The large energy gap between $^1O_2$ and ^{3}COM* could be conducive to energy transfer from ^{3}COM* to O_2 and it need to be studied furtherly.



Schematic R1. Deactivation Pathways for ^{3}COM* in the Presence of Oxygen (Rosario-Ortiz et al., 2016)

- Rosario-Ortiz, F. L., and Canonica, S.: Probe Compounds to Assess the Photochemical Activity of Dissolved Organic Matter, Environ. Sci. Technol., 50, 12532-12547, http://dx.doi.org/10.1021/acs.est.6b02776, 2016.

9) Implication section is short and lacks significance or contextualization in the large amount of literature on the photochemical oxidation of chromophoric organic matter in atmospheric aerosols.

We think that COM photolysis in aerosol and the effect of COM photolysis on aerosol aging is the most significant implication. However, these two points do not be emphasized in the section 4. The details are as follows.

"*We made a comprehensive study of COM photo-degradation, changes in optical properties and chemical compositions, COM photo-degradation affecting photochemical activity, and COM photo-degradation acting aerosol aging. The properties of COM photo-degradation were revealed. COM photo-degradation could be explained by reduction of carbonaceous components, decrease of light absorption capacity, and attenuation of fluorescence intensity. There are great differences in various COM in aerosols. Therefore, we suggested that the properties COM photo-degradation could be comprehensively characterized by carbonaceous components and optical characteristics. We studied that the photo-degradation could lead to COM decompose and change in types. High-molecular-weight DOM could be decomposed into low-molecular-weight DOM during photolysis. The conversion process of low-oxidation HULIS to high-oxidation HULIS is observed in ambient PM, which reflects the significant influence of photo-degradation on chemical composition. In turn, the attenuation and type conversion of COM provide an important basis to trace the aerosol aging process. Optical properties were also affected by COM photo-degradation.*

The effects of COM photo-degradation on the photochemical activity in aerosols are studied. We evaluated the effect of COM photo-degradation on the photochemical activity and the ability of triplet state generation and 1O2 yield was chosen to characterize the photochemical activity. Triplet

state generation ability remain unchanged in ambient PM and increased in POA during aerosol aging. On the one hand, only a small amount of chromophore could generate 3COM in aerosols. Thus, COM photo-degradation could not properly illustrate changes in 3COM*. On the other hand, the energy of capturing agents was closely related to measured 3COM* and TMP may capture short-lived triplet state. Therefore, chromophores, that could form a short-lived triplet state, may not be reduced or even generated during photolysis. Photo-degradation has a significant attenuating effect on the 1O2 yield. Therefore, photolysis and/or conversion of COM could be considered to be the main influence factor for photochemical reaction capacity. COM Photo-degradation indirectly affected the aerosols aging due to the changes in inducing reactive oxygen species. In addition, the photochemical reaction mechanisms and aerosol aging processes are relatively different in aerosols. It may be more useful to distinguish the types of 3COM* into high and low energies, so that the mechanism of COM photochemical reaction can be elucidated. In summary, the aerosol aging process has a remarkable impact on atmospheric photochemistry. Aerosol aging can not only change the type and content of COM, but also change their photochemical activity, which furtherly has a potential impact on the aerosol fate. Different types of aerosols have different aging mechanisms, so the environmental impacts caused by COM should also be different*".

Minor comments:

Chromophoric Organic Matters should be 'matter' instead of 'matters'. Consider how making this change will impact verb conjugation

We have corrected "*matters*" to "*matter*" in improved paper.

For example, we have corrected "*excited COM react with organic matters and promote secondary organic aerosols*" to "*excited COM react with organic matter and generate secondary organic aerosols*" in section 1 in the improved paper.

we have corrected "*Organic matters can be decomposed and transformed in aerosol due to illumination*" to "*Organic matter can be decomposed and transformed in aerosol due to illumination*" in section 3.1 in the improved paper.

Line 9: Change 'Furtherly' to 'Furthermore'

We have corrected "*Furtherly*" to "*Furthermore*" in the improved paper.

Line 12: Change 'particle' to 'particulate'

We have corrected "*particle*" to "*particulate*" in the improved paper.

Line 15: Change 'result also enunciate' to 'results also highlight'

We have corrected "*enunciate*" to "*highlight*" in the improved paper.

Line 30: Change 'improve' to 'is necessary for'

We have corrected "*improve*" to "*is necessary for*" in the improved paper.

Line 38: Change 'Photochemistry have' to 'Photochemistry has'

We have corrected "*Photochemistry have*" to "*Photochemistry has*" in the improved paper.

Line 101: Change 'time' to 'times'

We have corrected "*time*" to "*times*" in the improved paper.

Line 127: Change 'analyzed' to 'measured'

We have corrected "*analyzed*" to "*measured*" in the improved paper.

Line 131: Change 'excitation' to 'emission'

We have corrected "*excitation*" to "*emission*" in the improved paper.

Line 134: Change 'chromophores' to 'fluorophores'

We have corrected "*chromophores*" to "*fluorophores*" in the improved paper.

Line 176: Change 'photolysis' to 'photolyze' or rephrase sentence to 'undergo partial photolysis'

We have corrected "*partially photolysis*" to "*undergo partial photolysis*" in the improved paper.

Line 179: Change 'result' to 'results'

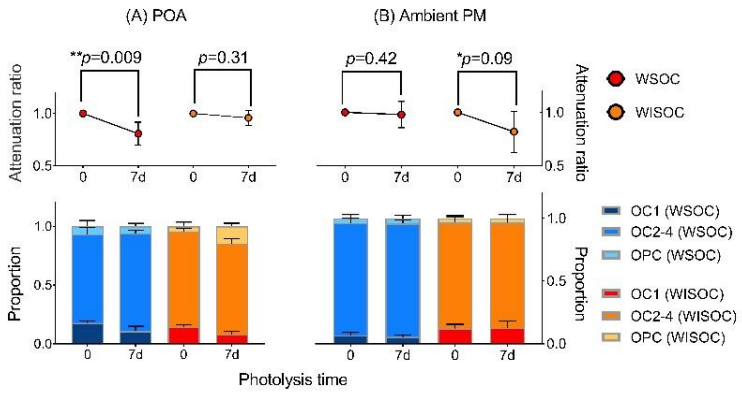
We have corrected "*result*" to "*results*" in the improved paper.

Line 186: Change 'Contrast with' to 'In contrast to'

We have corrected "*Contrast with*" to "*In contrast to*" in the improved paper.

Fig. 2b: Heading says 'Ambint PM' rather than 'Ambient PM'

We have corrected "*Ambint PM*" to "*Ambient PM*" in **Fig.2** in the improved paper.



Line194-195: Change 'represent an obvious decreasing trend due to aerosol photolysis' to 'significantly decrease during aerosol photolysis'

We have corrected "*represent an obvious decreasing trend due to aerosol photolysis*" to "*significantly decrease during aerosol photolysis*" in the improved paper.

Line 197: Change 'subduction' to 'decay

We have corrected "*subduction*" to "*decay*" in the improved paper.

Line 210: Change 'photolysis' to 'photolyze'

We have corrected "*photolysis*" to "*photolyze*" in the improved paper.

Line 208-210: Sentence that begins with 'The low attenuation result from COM' is unclear and needs revision

We have corrected "*The low attenuation result from COM have undergone a long-term atmospheric aging process and the water-soluble COM are easier to photolysis*" to "*The results suggest that COM have undergone a long-term atmospheric aging and water-soluble COM have greater ability to be photolyzed*" in the improved paper.

Line 219: Change 'chromophores' to 'fluorophores'

We have corrected "*chromophores*" to "*fluorophores*" in the improved paper.

Line 220: Change 'identified as' to 'associated with'

We have corrected "*identified as*" to "*associated with*" in the improved paper.

Line 243: Change 'show' to 'shows'

We have corrected "*show*" to "*shows*" in the improved paper.

Line 243: Change 'do not significant affect' to 'does not significantly affect'

We have corrected "*do not significant affect*" to "*does not significantly affect*" in the improved paper.

Line 260: Change 'through the approach of' to 'using'

We have corrected "*through the approach*" to "*using*" in the improved paper.

Line 261: Change 'EPRs' to 'EPR'

We have corrected "*EPRs*" to "*EPR*" in the improved paper.

Line 267: Change 'increase by 3 times' to 'increases by a factor of 3'

We have corrected "*increase by 3 times*" to "*increases by a factor of 3*" in the improved paper.

Line 277: Line 176: Change 'do' to 'does'

We have corrected "*do*" to "*does*" in the improved paper.

Line 278: Change 'The mechanism is same as' to 'The mechanism is the same as the'

We have corrected "*The mechanism is same as*" to "*The mechanism is the same as the*" in the improved paper.

Line 285: Change 'disappear' to 'disappears'

We have corrected "*disappear*" to "*disappears*" in the improved paper.

Line 288-289: Consider changing 'restraining' to 'attenuating' or 'inhibiting'. 'Restraining' is an odd word to use for this.

We have corrected "*restraining*" to "*attenuating*" in the improved paper.

Line 291: Change 'prove' to 'show'

We have corrected "*prove*" to "*show*" in the improved paper.

Line 293: Change 'prove' to 'study'

We have corrected "*prove*" to "*study*" in the improved paper.

Line 305: Change 'reflect' to 'reflects'

We have corrected "*reflect*" to "*reflects*" in the improved paper.