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Supplement of

Photodegradation of atmospheric chromophores: changes in oxidation state and photochemical reactivity

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Text S1. Calculation of optical characteristics of WSOM/MSOM

The mass absorption coefficient (MAE) of the extraction is calculated. Calculated formula as follows (Hems et al, 2020):

$$\text{MAE}\ (\text{m}^2 \cdot \text{g}^{-1}) = \frac{A(\lambda)\times\ln(10)}{C\times L} \quad (1)$$

In (1), A is the absorption of the extraction at the wavelength of 365 nm, *C* is the detected concentration of the extraction (μg/mL), and L is the path length of light (according to the cuvette, it is determined as 1 cm).

Absorption Ångström exponent is calculated (AAE) using the following calculation (Wu et al., 2019):

$$\text{AAE} = \frac{-\ln(A(\lambda_1)/A(\lambda_2))}{\ln(\lambda_1/\lambda_2)} \quad (2)$$

In (2), λ_1 and λ_2 are the selected wavelengths in the wavelength range with obvious wavelength-dependent characteristics.

E_2/E_3 is calculated using the following relation (Peuravuori & Pihlaja, 1997):

$$E_2/E_3 = MAE_{250}/MAE_{365} \quad (3)$$

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

$$a = 2.303A/l \quad (4)$$

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

Text S2. Calculation of dose of light by chemical method

According to the previous study (Laszakovits et al., 2017), 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. Calculated formula as follows：

$$I_\lambda = \frac{k'[PNA]_0 l}{1000\Phi(1-10^{-\varepsilon_\lambda l[PNA]_0})} \tag{5}$$

$$\Phi = 0.29[pyr] + 0.00029 \tag{6}$$

In (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 ($mol \cdot einstein^{-1}$).

Table S1. Details of primary organic aerosol (POA) and ambient particulate matter (ambient PM).

POA			Ambient PM			
Sample ID	**Sample category**	**Combustion quantity/g**	**Sample ID**	**Sampling Date**	**Sampling Season**	**Illustration**
1	Wheat Straw	2.4860	9	2017-4-18	Spring	Sand Storm
2		2.4869	10	2017-4-19		
3	Corn Straw	2.4865	11	2017-1-3	Winter	Heavy pollution
4		2.4863	12	2019-1-4		
5	Rice Straw	2.4873	13	2017-7-3	Summer	Good Air Quality
6		2.4870	14	2017-7-4		
7	Wood	5.0364	15	2017-11-5	Autumn	Slight pollution
8		5.0326	16	2019-11-6		

Table S2. OC concentration of samples for optical analysis.

POA				Ambient PM			
Sample ID	c_{WSOC}/ppm	c_{MSOC}/ppm	Dilution factor (WSOC/MSOC)	Sample ID	c_{WSOC}/ppm	c_{MSOC}/ppm	Dilution factor (WSOC/MSOC)
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_{MSOC}/ppm	**Dilution factor (WSOC/MSOC)**	**Sample ID**	c_{WSOC}/ppm	c_{MSOC}/ppm	**Dilution factor (WSOC/MSOC)**
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

Table S3. Concentration of water-soluble organic carbon (WSOC) exaction for triplet state formation experiment.

POA		Ambient PM	
Sample ID	**c_{WSOC}/ppm**	**Sample ID**	**c_{WSOC}/ppm**
1-0h	14.98	9-0h	14.78
1-7d	15.01	9-7d	15.82
2-0h	14.40	10-0h	13.25
2-7d	13.24	10-7d	13.43
3-0h	16.73	11-0h	16.56
3-7d	13.44	11-7d	13.35
4-0h	16.89	12-0h	14.14
4-7d	13.15	12-7d	14.60
5-0h	16.75	13-0h	14.92
5-7d	14.70	13-7d	14.00
6-0h	14.95	14-0h	14.53
6-7d	14.57	14-7d	12.29
7-0h	19.33	15-0h	10.56
7-7d	15.92	15-7d	8.42
8-0h	18.87	16-0h	9.67
8-7d	14.18	16-7d	12.61

Table S4. Proportion of COM in POA.

		WSOM				MSOM			
		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				MSOM			
		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

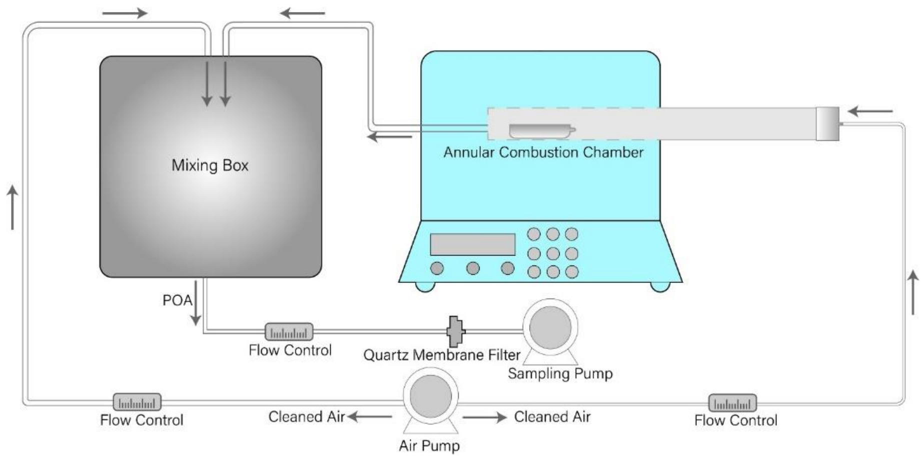

Figure S1. Schematic diagrams of combustion equipment for POA. Wheat straw, corn straw, rice straw and wood were burned in the annular combustion chamber when temperatures rose to 500 ℃. The clean air was introduced at a flow rate of 2 L/min to ensure complete combustion. The clean air was also introduced into mixing box at a flow rate of 2 m3/h to dilute the combustion gas. POA samples were collected on the quartz filter (a diameter of 37 mm, Pall life sciences, Pall Corporation, America).

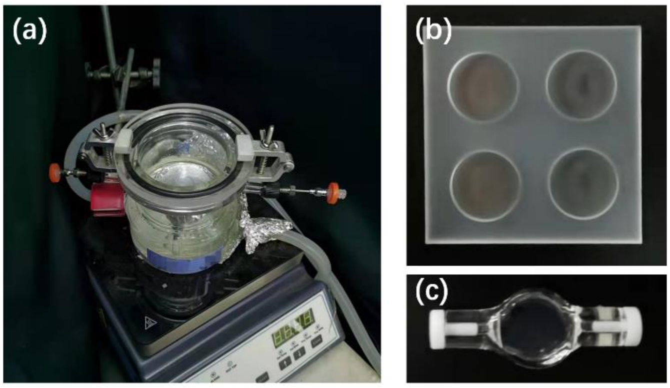

Figure S2. Schematic diagrams of the photochemical devices. (a) The reactor is used for maintaining the reaction environment. (b) The capsule is used for the experiment of triplet state inducing singlet oxygen. The size of quartz plate is 35×35 mm^2. The size of the tanks is a radius of 5.6 mm and a 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 reactor was sealed through clamping a quartz cover to reactor. 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 constant in the reactor. The reactor was placed on a magnetic stirrer with a rotation speed of 200 rmp. A xenon lamp was equipped with a VISREF light filter (PLS-SXE 300, Perfectlight, China) to simulate sunlight (The wavelength spectrum of the xenon lamp is shown in **Figure S3**).

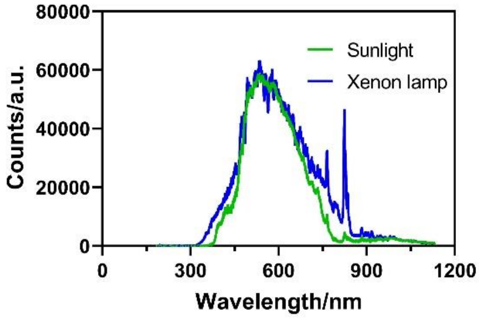

Figure S3. Wavelength spectrum of Xenon lamp. Relative irradiance data of xenon lamp is from perfect light Inc. Relative irradiance data of sunlight is from *The Tropospheric Visible Ultra-Violet (TUV) model web page.* Input parameters for the TUV model were: Longitude: E108°58′34.58″, Latitude: N34°22′35.07″, measurement altitude: 0.02 km, surface albedo: 0.1, aerosol optical depth: 0.235, cloud optical depth: 0.00.

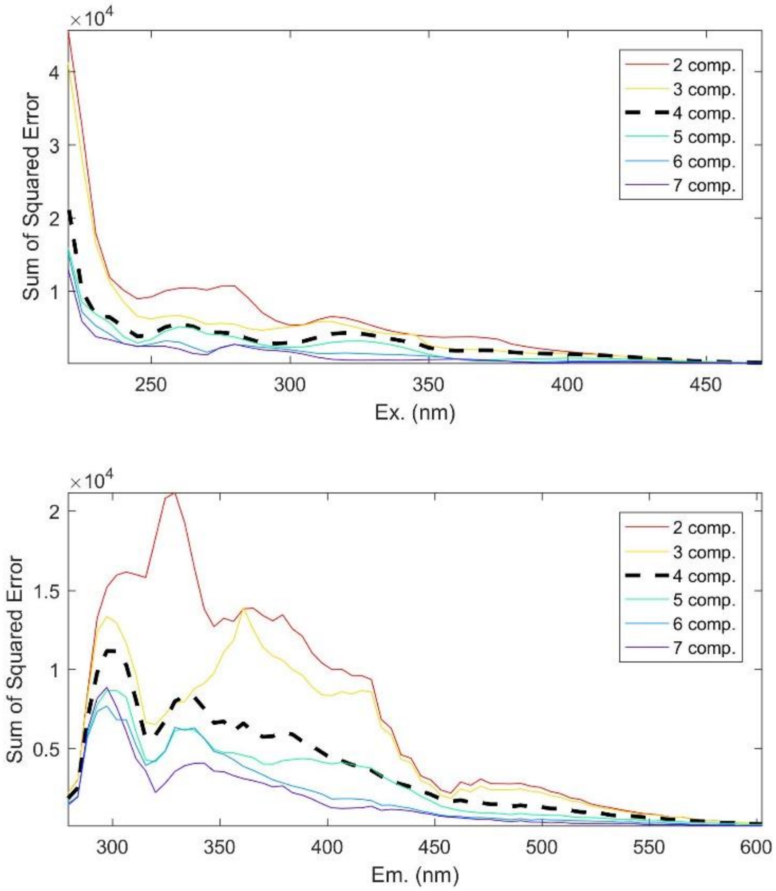

Figure S4. Analysis error of PARAFAC model.

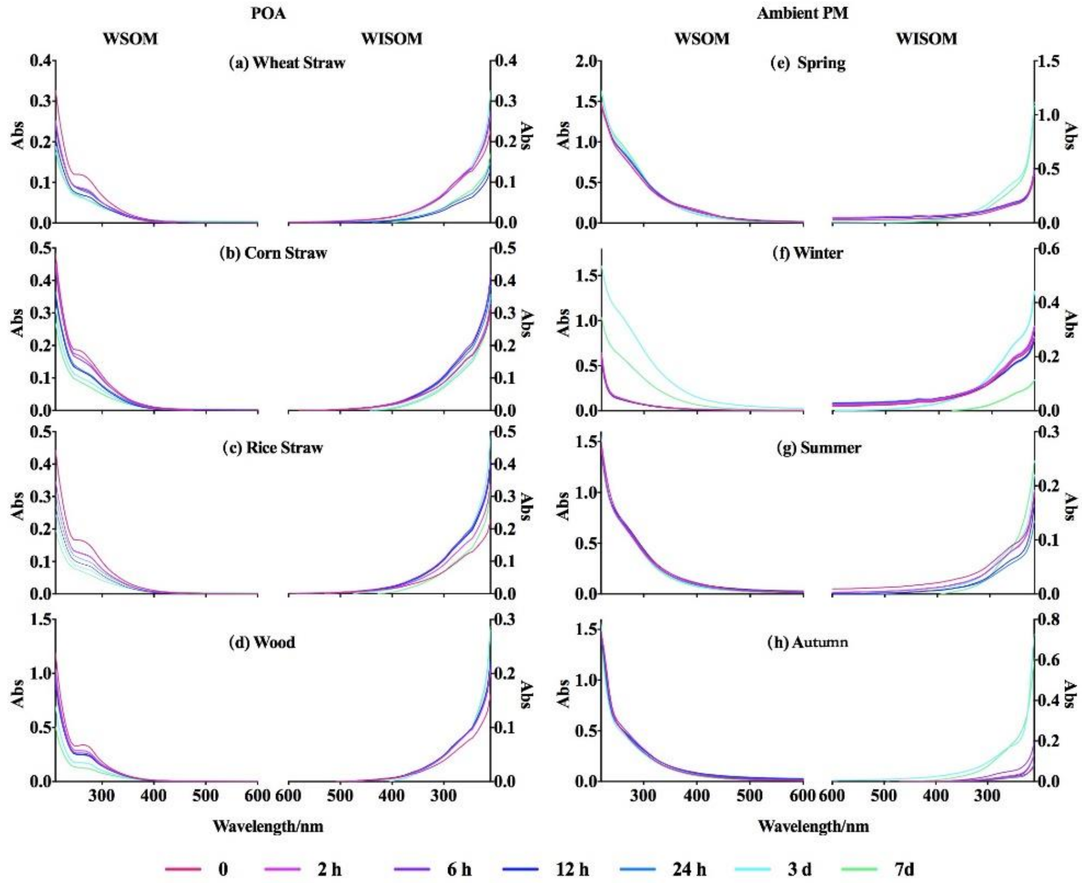

Figure S5. Absorption spectra of POA and ambient PM during the photo-aging process.

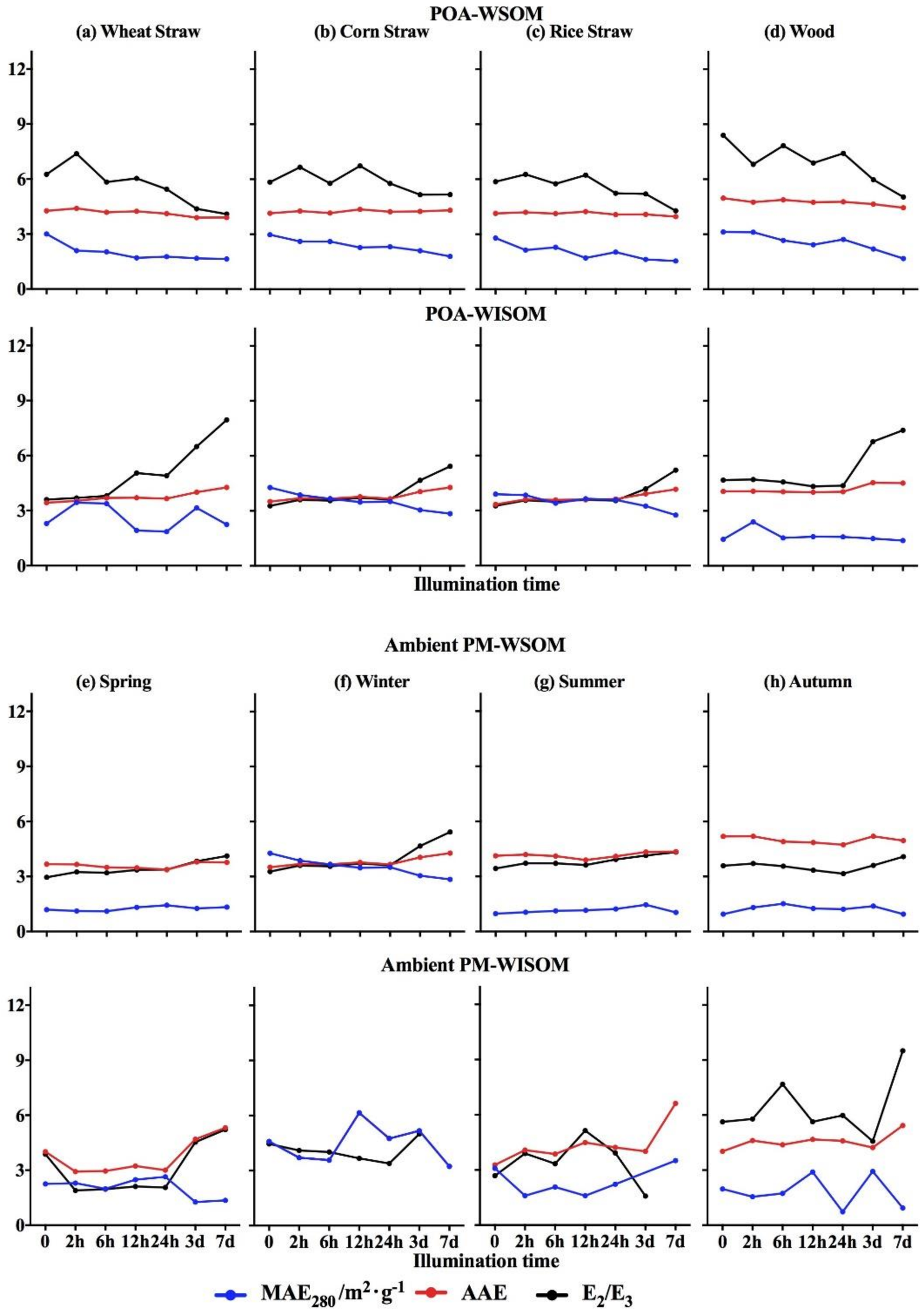

Figure S6. Optical characteristics of E_2/E_3, AAE and MAE of POA and ambient PM.

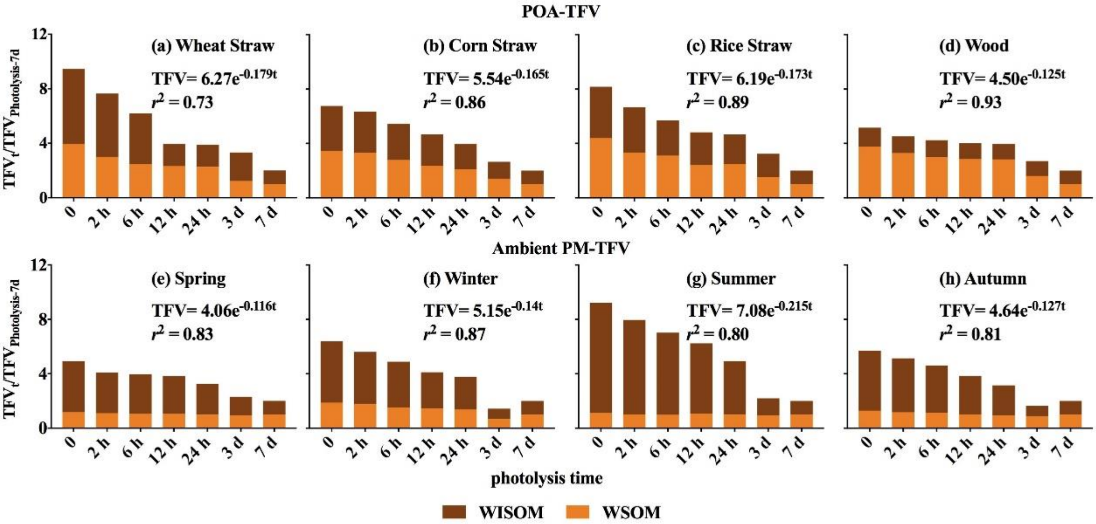

Figure S7. Characteristic of fluorescence volume attenuation in POA and ambient PM samples during the photodegradation process.

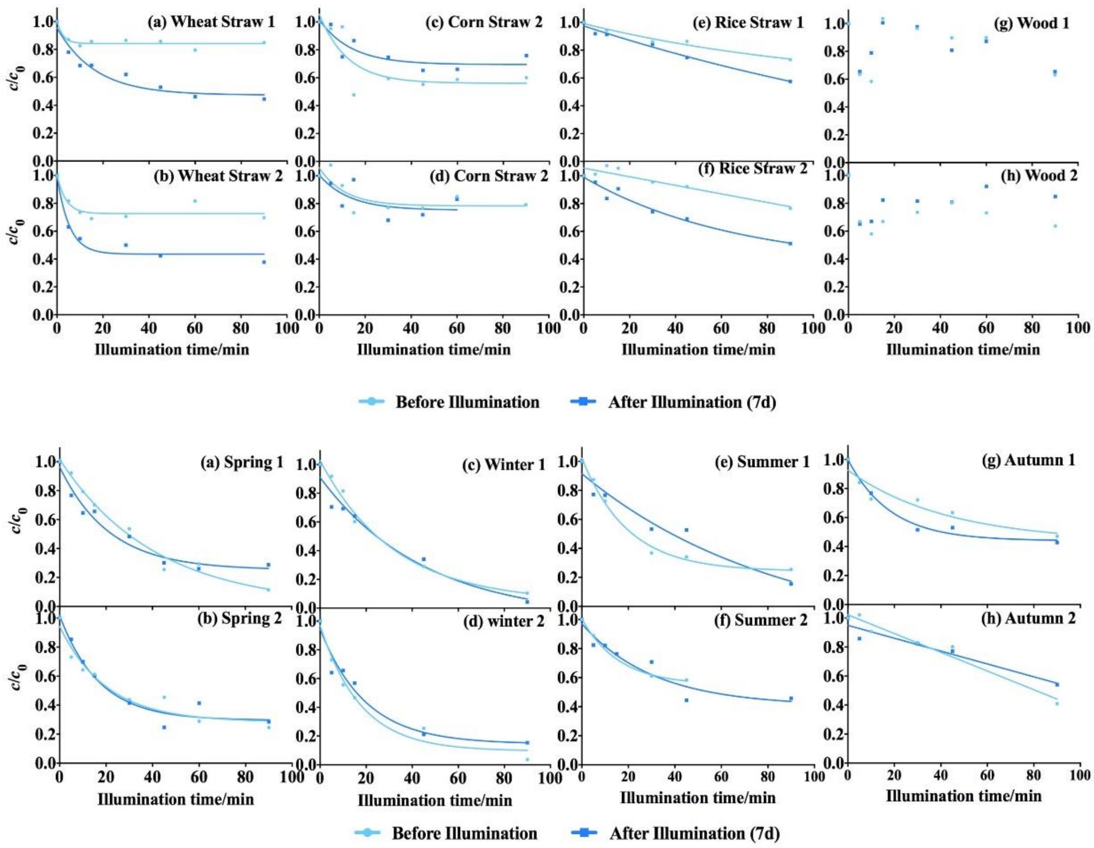

Figure S8. Formation characteristic of triplet state of POA and ambient PM samples.

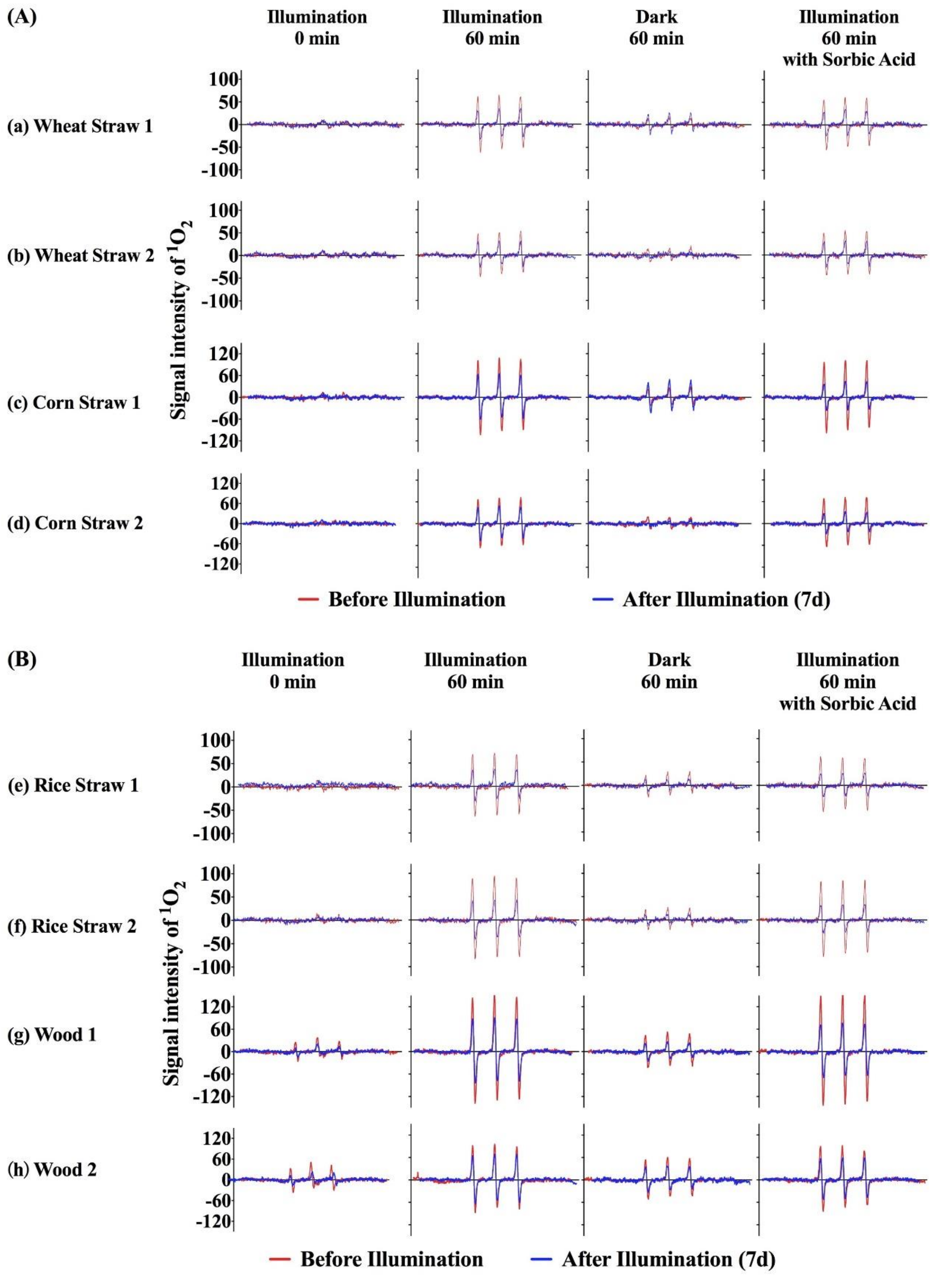

Figure S9. Characteristic of ^{3}CDOM* formation of POA driving $^1O_2$.

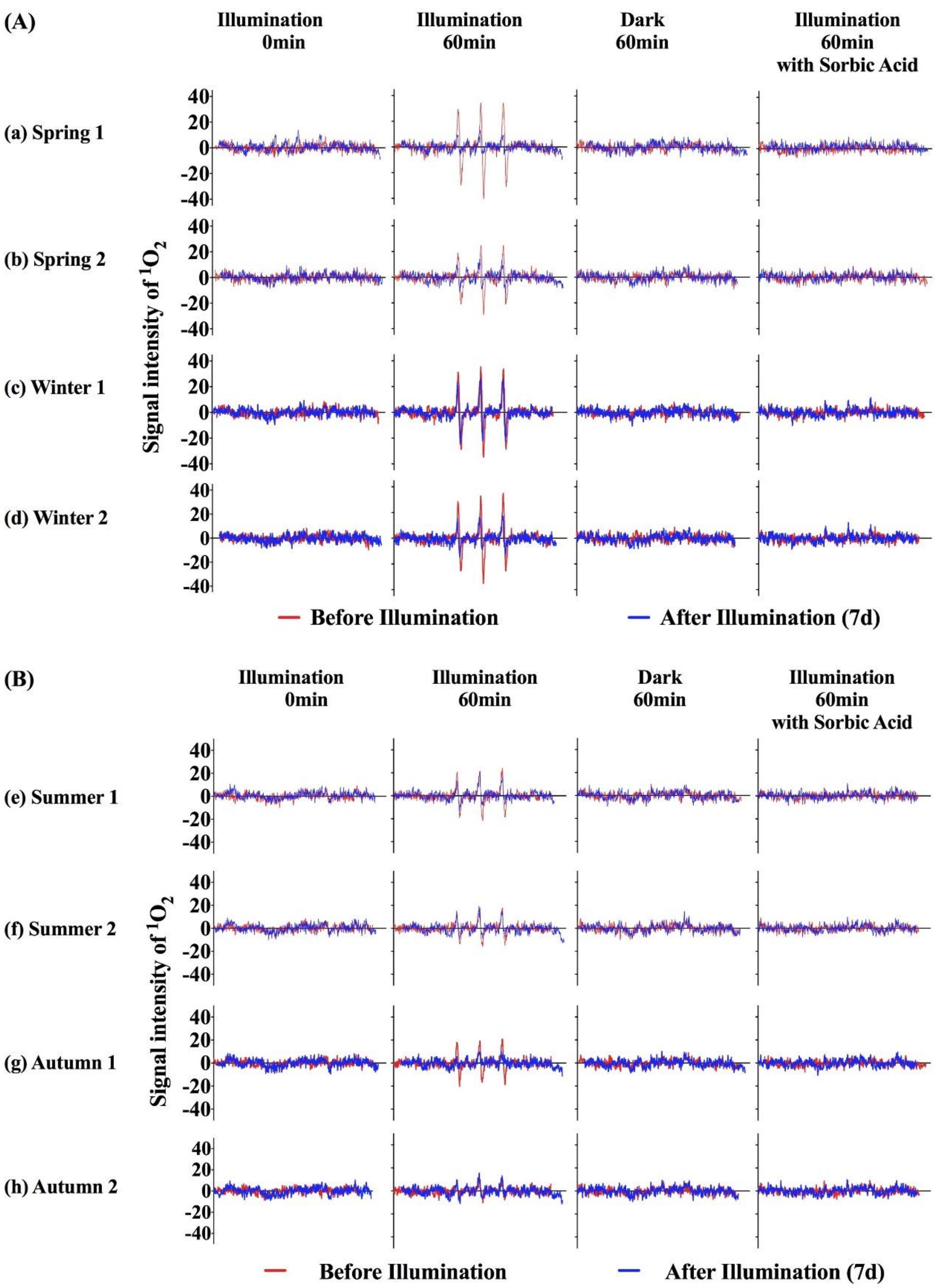

Figure S10. Characteristic of $^3CDOM^*$ formation of ambient PM driving $^1O_2$.

References:

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.

Hems, R. F.; Schnitzler, E. G.; Bastawrous, M.; Soong, R.; Simpson, A. J.; Abbatt, J. P. D.: Aqueous Photoreactions of Wood Smoke Brown Carbon, *ACS Earth Space Chem.*, *4*, 1149-1160, https://doi.org/10.1021/acsearthspacechem.0c00117 2020.

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.

Peuravuori, J., Pihlaja, K.: Molecular size distribution and spectroscopic properties of aquatic humic substances, *Anal. Chim. Acta*, *337*, 133-149, https://doi.org/10.1016/S0003-2670(96)00412-6, 1997.

Wu, G.; Fu, P.; Ram, K.; Song, J.; Chen, Q.; Kawamura, K.; Wan, X.; Kang, S.; Wang, X.; Laskin, A.; Cong, Z.: Fluorescence characteristics of water-soluble organic carbon in atmospheric aerosol, *Environ. Pollut.*, *268*, 115906, https://doi.org/10.1016/j.envpol.2020.115906, 2021.