Supporting Information

Triplet State Formation of Chromophoric Dissolved Organic Matter in Atmospheric Aerosols: Characteristics and implications

Qingcai Chen,[a]* Zhen Mu,[a] Xu Li,[b] Mamin Wang,[a] Jin Wang,[c] Ming Shan,[d] Xudong Yang,[d] Xingjun Fan,[e] Jianzhong Song,[f] Yuqin Wang,[a] Pengchuan Lin,[g] Lixin Zhang,[a] Zhenxing Shen,[h] Lin Du[b]*

[a] *School of Environmental Science and Engineering, Shaanxi University of Science and Technology, Xi'an 710021, China*
[b] *Environment Research Institute, Shandong University, Qingdao, 266237, China*
[c] *School of Civil Engineering, Beijing Jiaotong University, Beijing 100044, China*
[d] *Department of Building Science, School of Architecture, Tsinghua University, Beijing, 100084, China*
[e] *College of Resource and Environment, Anhui Science and Technology University, 233100 Anhui, China*
[f] *State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China*
[g] *College of Resources and Environment, University of Chinese Academy of Sciences, 100190, Beijing, China*
[h] *Department of Environmental Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, China*

*Corresponding authors:
*(Q. C.) Phone: (+86) 0029-86132765; e-mail: chenqingcai@sust.edu.cn; School of Environmental Science and Engineering, Shaanxi University of Science and Technology, Weiyang District, Xi'an, Shaanxi, 710021, China;
*(L. D.) Phone: (+86) 0532-58631980; e-mail: lindu@sdu.edu.cn; Environment Research Institute, Shandong University, Qingdao, 266237, China

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Text S1. Calculation of the formation rate of triplet states.

The chromophoric dissolved organic matter (CDOM) forms triplet states (^{3}CDOM*) under solar illumination. The reaction rate between ^{3}CDOM* and TMP is characterized by R. the reaction rate R can be expressed as (1).

$$R=k_0[\mathrm{TMP}][^3\mathrm{CDOM}^*] \tag{1}$$

where k_0 is the reaction rate constant. [TMP] is the concentration of TMP. [^{3}CDOM*] is the steady state concentration of ^{3}CDOM*. Similar to equation (1), the reaction rate of TMP can be expressed by equation (2) (Bodhipaksha, et al., 2015; Canonica & Hoigné, et al., 1995).

$$R_{\mathrm{TMP}}=k_{\mathrm{TMP}}[\mathrm{TMP}][^3\mathrm{CDOM}^*]=k'_{\mathrm{TMP}}[\mathrm{TMP}] \tag{2}$$

where k_{TMP} is the reaction rate constant of TMP.

$$[^3\mathrm{CDOM}^*]=k_f/k_e=[\mathrm{OC}]I_{\mathrm{BrC}}/k_e \tag{3}$$

where k_f is formation rate constants of triplet states, which is characterized by the concentration of CDOM with the ability to form ^{3}CDOM*. The ^{3}CDOM* is self-quenching through producing phosphorescence, or by reacting with TMP or eliminating by other means. k_e is the total quenching rate of ^{3}CDOM* through various paths (Sharpless, 2012). [OC] is the concentration of organic carbon (OC) in the reaction system, and I_{BrC} is the concentration coefficient of CDOM. I_{BrC} of ambient PM is 13% (Feng, et al., 2013). [^{3}CDOM*] is not the absolute concentration of ^{3}CDOM*, but it is the relative concentration that quenching rate of CDOM which is characterized by attenuation rate of TMP combined with water-soluble organic carbon (WSOC) concentration.

Text S2. Calculation of consumption rate in reactor equivalent to aerosol.

The formation rate of ^{3}CDOM* is related to the intensity of illumination (The difference between xenon lamp and solar illumination) and the volume of aerosol (The difference between solution volume and atmospheric aerosol volume). The parameters in the reactor are converted to those in aerosol.

$$E_0 = I_0(1 - 10^{k l_0 c_0})S_0 \tag{4}$$

where E_0 is reaction conditional coefficient in reactor. I_0 is the illumination intensity of xenon lamp. k is the mass absorption efficiency (MAE) of aerosol. l_0 is xenon lamp light passing distance in solution. S_0 is illumination area of solution in reactor, c_0 is WSOC extraction concentration in reactor. The volume of extraction in the reactor is (150×10^{-9}) m^3. The direct illuminated area S_0 is $\pi \times (5.6\times10^{-3})^2$ m^2. The distance of light passes through the solution in the reactor is $(150\times10^{-9})/[\pi\times (5.6\times10^{-3}\pi)^2\ ]$ m. Table S1-S3 show details of reaction concentration of extraction.

$$E_1 = I_1(1 - 10^{k l_1 c_1})S_1 \tag{5}$$

In the equation (5), E_1 is reaction conditional coefficient in aerosol. I_1 is the illumination intensity of solar illumination. k is the MAE of aerosol, which is the same as that in the reactor. l_0 is distance of solar light passing through aerosols of unit volume. S_0 is direct illumination area of unit aerosol, c_0 is OC concentration in aerosol. In order to estimate the ability of CDOM to form ^{3}CDOM* in aerosol under solar illumination, the reaction concentration and illumination intensity of xenon lamp in the reactor were equivalent to the concentration of the same mass of WSOC in the 1 m^3 aerosol and illumination intensity of solar illumination. In the 1 m^3 aerosol, the direct illuminated area is 1 m^2, the distance of light passing through 1 m^3 aerosol is 1 m, and the concentration of OC in aerosol is $(150\times10^{-9})*c_0$.

$$E_1 = \left\{\frac{I_1}{I_0} \times \frac{1-10^{(1.5\times10^{-7})kc}}{[(5.6\times10^{-3})^2\times\pi]\left[1-10^{\left(\frac{1.5\times10^{-7}}{5.6\times10^{-3}\times\pi}\right)^2 kc}\right]}\right\} \times E_0 \tag{6}$$

Therefore, there is a coefficient λ to transfers the equivalent of reaction conditions in reactor to aerosol as

$$\lambda = \left\{ \frac{I_1}{I_0} \times \frac{1-10^{\left(1.5\times10^{-7}\right)kc}}{\left[\left(5.6\times10^{-3}\right)^2\times\pi\right]\left[1-10^{\left(\frac{1.5\times10^{-7}}{5.6\times10^{-3}\times\pi}\right)^2 kc}\right]} \right\} \tag{8}$$

In aerosols, the rate of ^{3}CDOM* formation is characterized as

$$k_a = \frac{k_s}{\lambda}[\mathrm{OC}] \tag{7}$$

where k_s the average reaction rate of TMP in the reactor, [OC] is the atmospheric concentration of OC and the unit is ug/m^3. k_a is the average reaction rate of TMP in aerosol and the unit is mol/(m^3•min).

Table S1. Sample source, reaction concentration, reaction rate constant triplet states formation rate in aerosols of ambient particulate matter.

	Season	Sampling date	WSOC (mg L^{-1})	k_{TMP}/(min^{-1})	$PM_{2.5}$ (μg m^3)	$^3CDOM^*$ (μmol m^{-3} h^{-1})
1	Winter	2017/12/1	24.01	0.02854	132	139.55
2		2017/12/2	41.87	0.03987	121	89.40
3		2017/12/4	33.06	0.0397	154	291.92
4		2017/12/5	29.70	0.04151	96	112.40
5		2017/12/6	27.75	0.0368	76	124.23
6		2017/12/7	37.57	0.04039	94	110.04
7		2017/12/8	25.67	0.04319	95	117.23
8		2017/12/9	22.31	0.04017	30	105.87
9		2017/12/10	28.16	0.03565	76	133.91
10		2017/12/11	27.75	0.04587	59	194.31
11		2017/12/12	36.56	0.03726	92	116.24
12		2017/12/13	35.42	0.04558	109	105.61
13	Summer	2017/6/24	24.95	0.02134	19	153.69
14		2017/6/25	27.52	0.02596	25	143.88
15		2017/6/26	28.65	0.02661	29	131.62
16		2017/6/27	32.28	0.02437	42	108.18
17		2017/6/28	26.46	0.0157	35	87.82
18		2017/6/29	26.81	0.02243	32	121.96
19		2017/6/30	28.32	0.01802	25	91.17
20		2017/7/1	32.10	0.01927	32	84.16
21		2017/7/2	32.86	0.01978	47	80.83
22		2017/7/3	39.43	0.02217	52	116.70
23		2017/7/4	32.93	0.01837	53	103.90
24		2017/7/5	26.66	0.01222	50	52.91

Table S2. Sample source, reaction concentration and reaction rate constant of primary organic aerosol.

	Category	Source	WSOC (mg/L)	k_{TMP} (min^{-1})
1	Straw Burning	Wheat straw	105.42	0.00593
2		Corn straw1	132.89	0.00504
3		Corn straw 2	111.42	0.01311
4		Corn straw 3	17.87	0.03271
5		Rice straw	32.17	0.05126
6		Artemisia straw 1	46.32	0.03154
7		Artemisia straw 2	32.53	0.05086
8		Straw rod compaction 1	37.16	0.04138
9		Straw rod compaction 2	42.44	0.08779
10	Wood Burning	Pine wood 1	35.31	0.00905
11		Pine wood 2	32.58	0.00691
12		Chinese fir	95.21	0.00526
13		Wood 1	48.36	0.0327
14		Wood 2	21.55	0.05842
15		Grape branches 1	25.74	0.149
16		Grape branches 2	32.12	0.07909
17	Coal Combustion	Coal combustion 1	44.85	0.01059
18		Coal combustion 2	18.33	0.05905
19		Coal combustion 3	15.17	0.0432
20		Coal combustion 4	30.13	0.06968
21	Vehicle	Medium-sized general wagon 1	11.29	0.01201
22		Medium-sized general wagon 2	12.92	0.0286
23		Heavy general truck 1	14.91	0.01106
24		Heavy general truck 2	9.60	0.01254
25		Bus 1	14.25	0.01185
26		Bus 2	13.02	0.00653
27	Cooking	Scrambled egg with tomato (Liquefied petroleum gas)	14.71	0.00594
28		Fried meat (Liquefied petroleum gas)	11.44	0.0046
29		Roast mutton, photo and squid (charcoal)	38.96	0.01668
30		Roast duck 1 (Wood)	42.18	0.01116
31		Roast duck 2 (Wood)	40.19	0.03471

Table S3. Sample source, reaction concentration and reaction rate constant of secondary organic aerosol.

	Categories of oxidation	Precursors		Oxidation conditions	WSOC (mg/L)	k_{TMP} (min^{-1})
1	Primary Oxidation	APIN	2 ppm	O_3/OH Scavenger/No Light	50.41	0.0232
2					30.76	0.03503
3		LIM	2 ppm	O_3/OH Scavenger/No Light	29.70	0.02307
4					39.13	0.03182
5	Moderate Oxidation	NAP	——	NO_X/OH	40.99	0.034
6					30.47	0.03484
7					17.71	0.02645
8					31.20	0.04028
9		APIN	2 ppm	NO_X/OH	32.61	0.03158
10					31.65	0.02726
11		LIM	2 ppm	NO_X/OH	19.82	0.02569
12					30.27	0.02757
13		TOL	2 ppm	NO_X/OH	4.39	0.02797
14					28.78	0.02478
15		TOL	2 ppm	NO_X	29.39	0.03091
16					52.32	0.03707
17	Over Oxidation	APIN	2 ppm	Excess O3/Light	41.78	0.02456
18					31.20	0.02377
19		APIN	2 ppm	Excess O3	39.79	0.02922
20					30.39	0.03015
21		LIM	2 ppm	Excess O3	42.11	0.0385
22					30.65	0.02964

Table S4. The full names correspond to acronyms in the paper.

Full names	Acronyms
chromophore dissolved organic matter	CDOM
triplet-state chromophoric dissolved organic matter	^{3}CDOM*
singlet oxygen	$^1O_2$
hydroxyl radical	•OH
reactive oxygen species	ROS
excitation-emission matrices spectra	EEMs
secondary organic aerosol	SOA
sorbic acid	SA
2,4,6-trimethylphenol	TMP
primary organic aerosol	POA
ambient particulate matter	Ambient PM
water-soluble organic matter	WSOM
water-soluble organic carbon	WSOC
total organic carbon	TOC
electron paramagnetic resonance	EPR
5,5-dimethyl-1-pyrroline-N-oxide	DMPO
2,2,6,6-tetramethyl-piperidine	TEMP
absorption Angström-exponent	AAE
mass absorption efficiency	MAE
Abs_{250nm}/Abs_{365nm}	E_2/E_3
Low-oxidation conditions	LO
Moderate-oxidation conditions	MO
High-oxidation conditions	HO
limonene	LIM
α-pinene	APIN
toluene	TOL
naphthalene	NAP

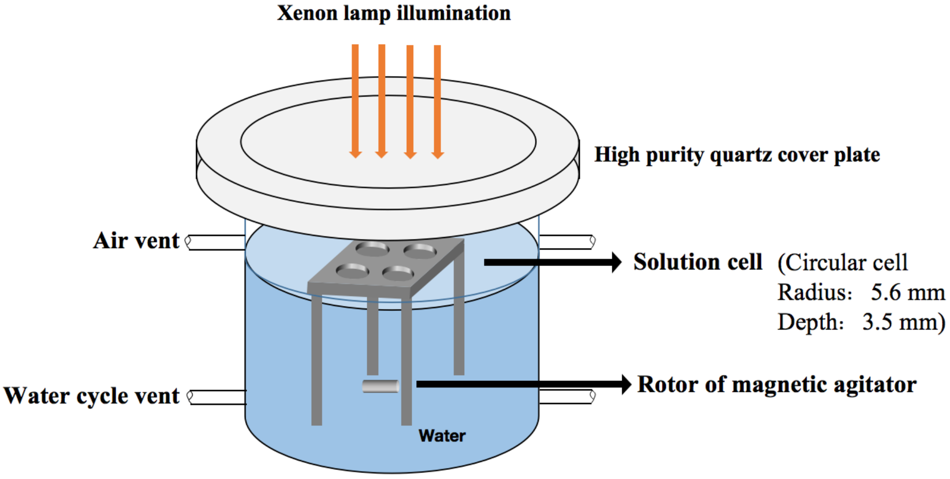

Figure S1. Photochemistry reaction device. In the process of illumination, the reactor is placed on the magnetic agitator with a rotational speed of 200 rmp. The reactor is connected with a water-cooled circulator to ensure that the water temperature in the reactor is constant and the water temperature is set to 8 ℃. The temperature in the reactor is 25 ℃.

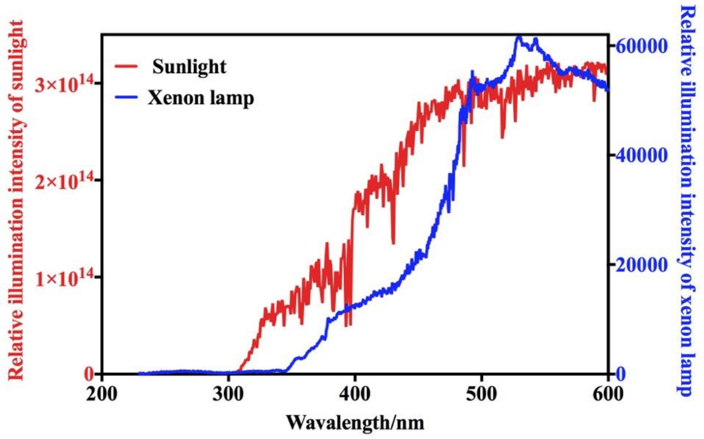

Figure S2. Wavelength spectrum of Xenon lamp. Relative irradiance data of xenon lamp is from perfectlight Inc. Relative irradiance data of sunlight is from *The Tropospheric Visible Ultra-Violet (TUV) model web page*. Input parameters for the TUV model were: Longitude: E108°58′34.58″, Latitude: N34°22′35.07″, measurement altitude: 0.02 km, surface albedo: 0.1, aerosol optical depth: 0.235, cloud optical depth: 0.00.

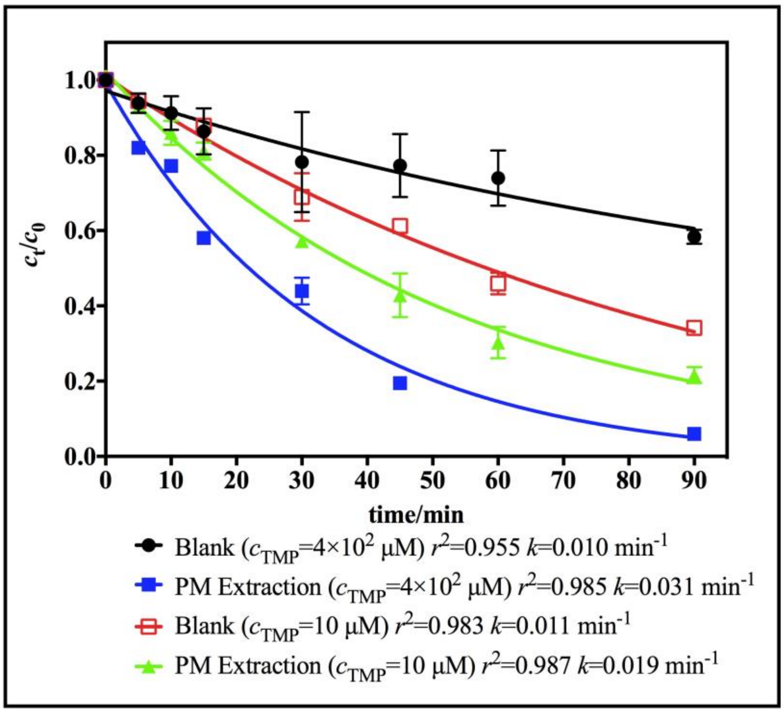

Figure S3. The attenuation rate of TMP with different DOM concentration.

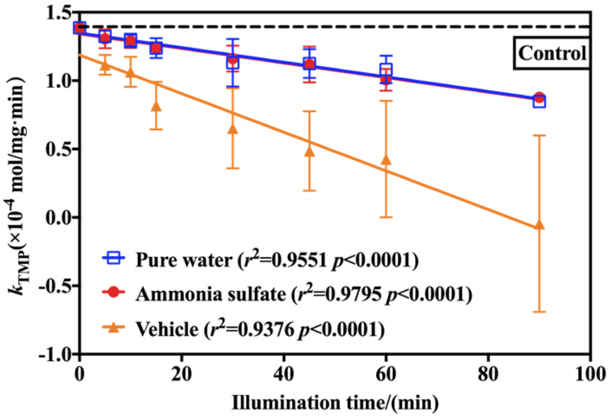

Figure S4. Background of ultra-pure water and ammonium sulfate. The photochemistry reaction of ammonium sulfate solution (n = 3) with ultra-pure water (n = 3) is described. The consumption rate of TMP by ammonium sulfate solution ($c_{\text{ammonium sulfate}}$ = 4×10^{-3} mol/L) and ultra-pure water conforms to the first-order reaction kinetics and the consumption rate is basically the same, that is, the sulfate radical groups formed by sulfates in particulate matter have no obvious effect on TMP consumption. There should be self-quenching effect. The minimum reaction rate constant of aerosols from different sources is motor vehicle exhaust samples (n = 6). The figure shows that there are obvious differences between motor vehicle exhaust and blank sample, so the effect of self-quenching effect is acceptable.

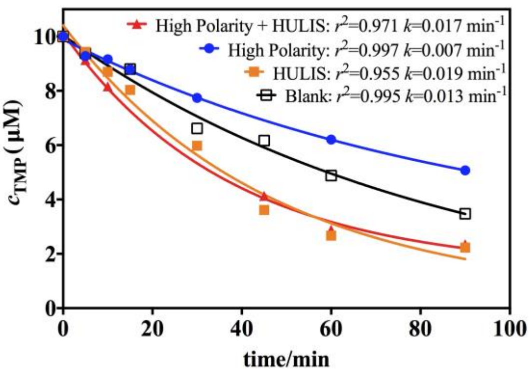

Figure S5. Effect of salts separated from PM extraction on triplet state formation. According to the above experiments, we insist that the salts from the extractions of aerosol has no significant effect on TMP consumption.

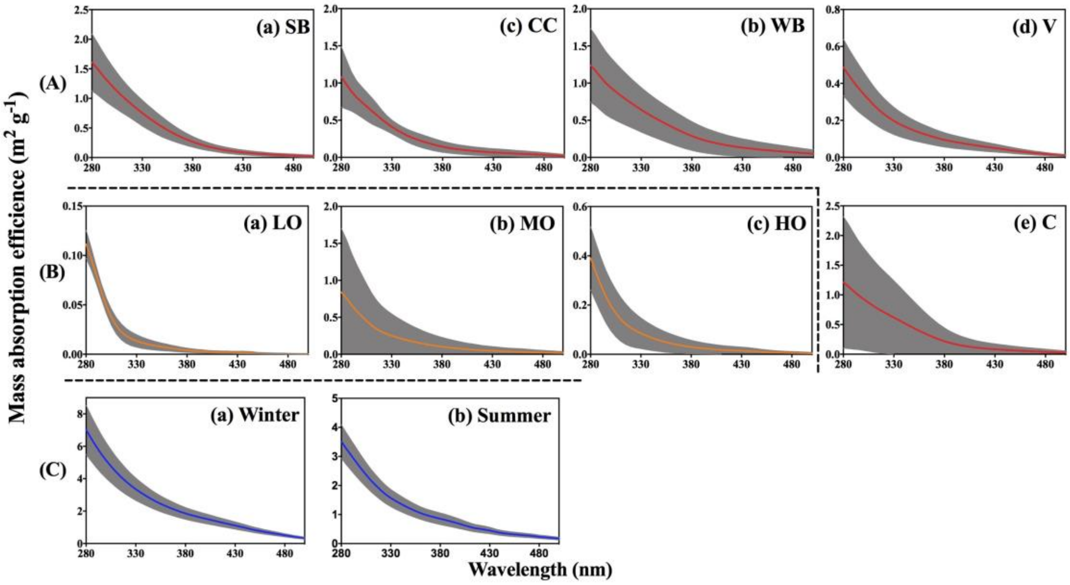

Figure S6. UV−visible absorbance spectra of the samples. (A) POA. (a) Straw Burning, (b) Coal Combustion, (c) Wood Burning, (d) Vehicle, (e) Cooking. (B) SOA. (a) Low-Oxidation, (b) Moderate-Oxidation, (c) High-Oxidation. (C) Ambient PM. (a) Winter, (b) Summer.

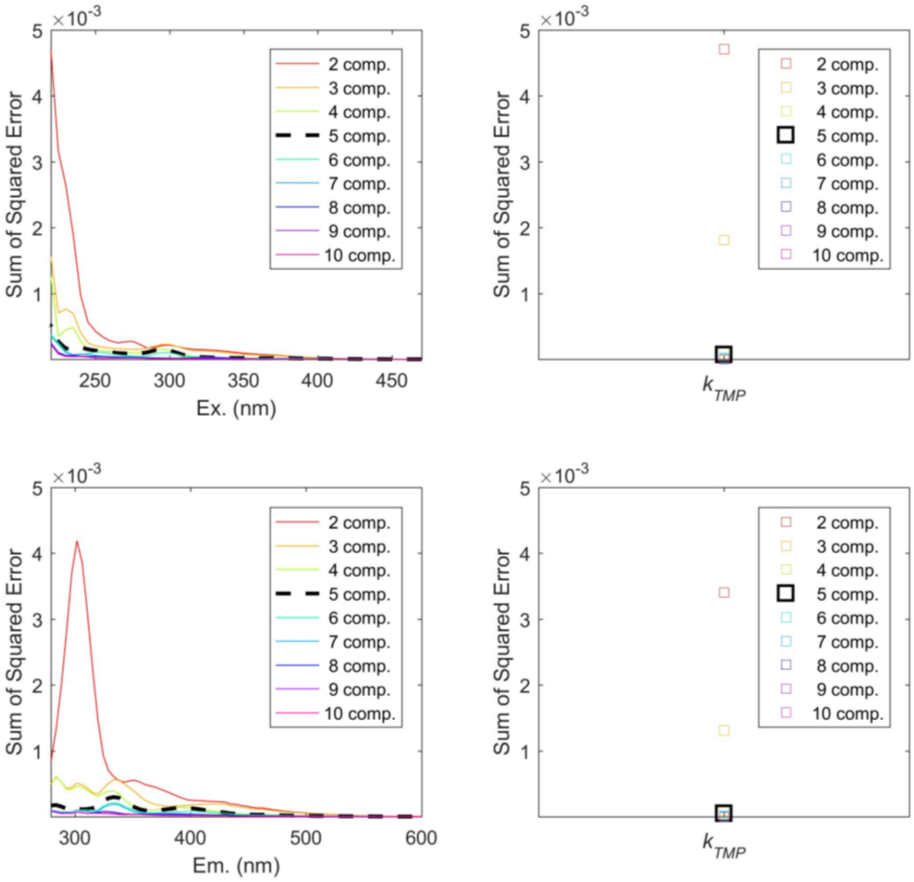

Figure S7. Error comparison of C2 - C10 model in PARAFAC analysis. The black dotted line represents the number of factors.

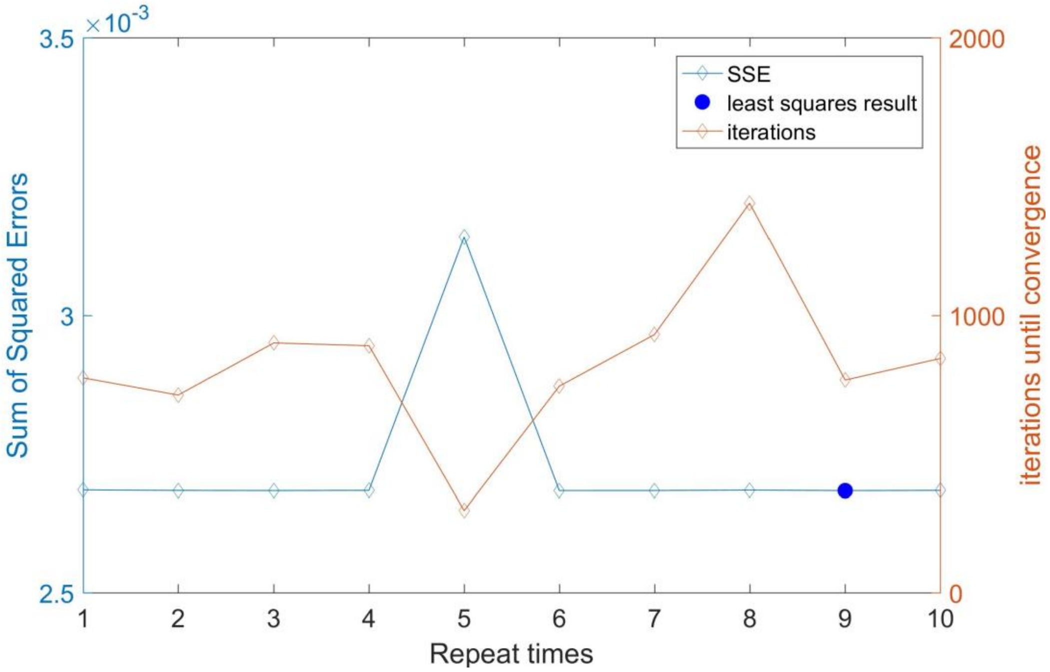

Figure S8. Comparisons of 10 repeat runs of 5 component model.

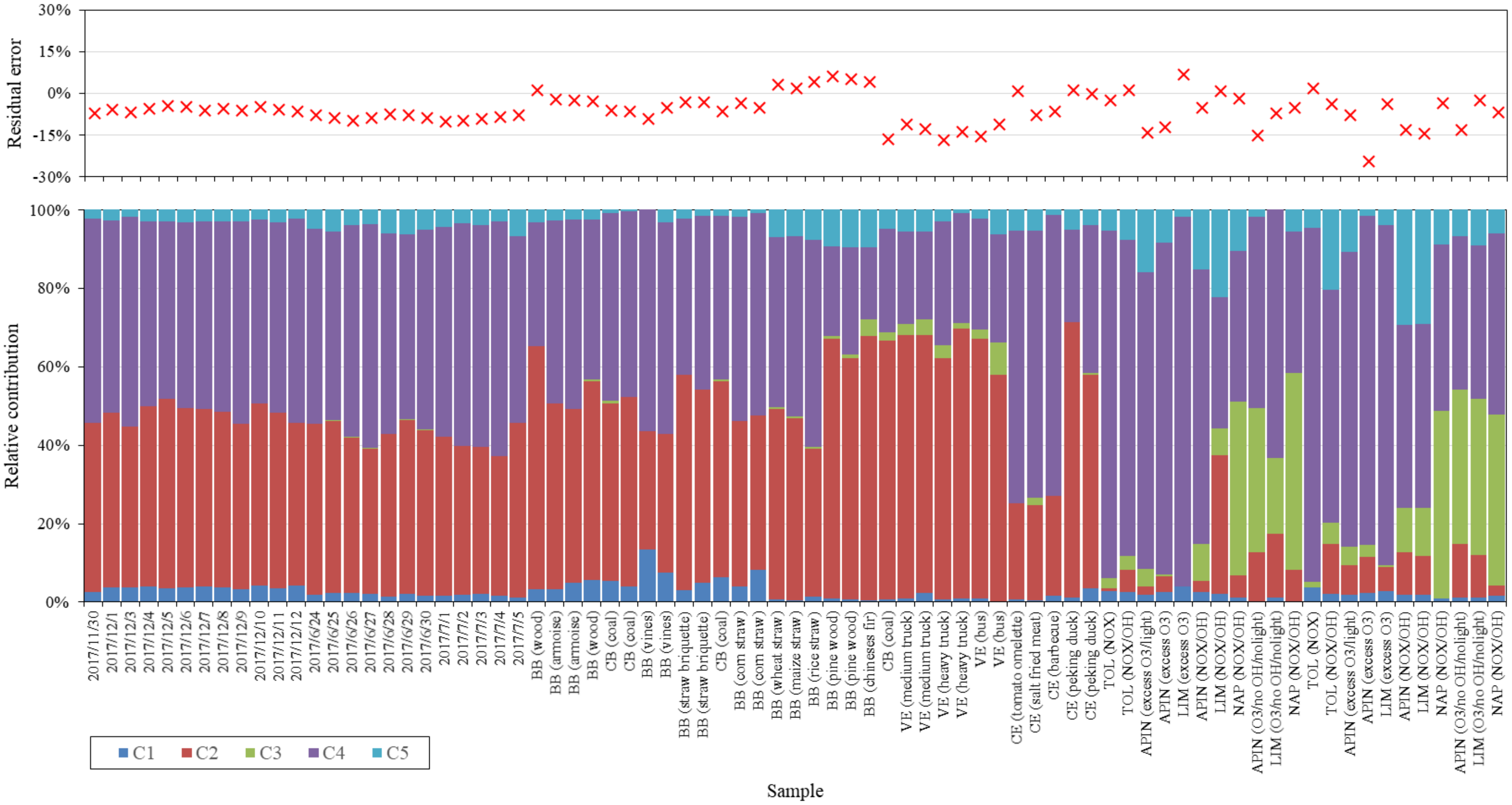

Figure S9. Relative contribution of fluorescence and residual of model.

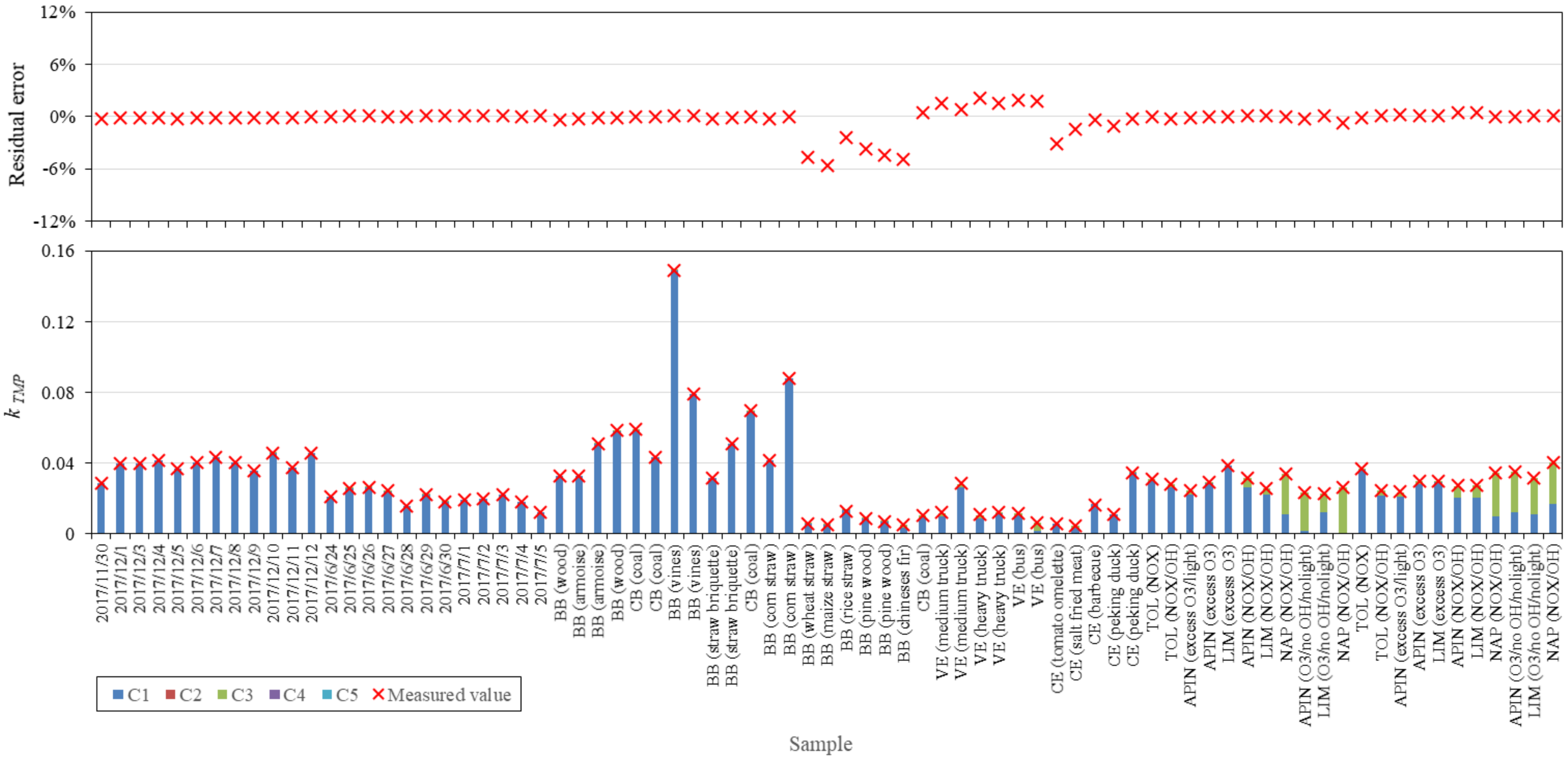

Figure S10. Contribution of CDOM to k_{TMP} and residual of model.

References

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