Photo~~-~~degradation of ~~atmospheric~~ Atmospheric ~~chromophores~~Chromophores: ~~type conversion and c~~Changes in Oxidation State and ~~photochemical~~ Photochemical ~~reactivity~~Reactivity

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Abstract: Atmospheric chromophoric organic matter~~s~~ (COM) can participate in photochemical reactions because of the photosensitiveness, thus COM have a potential contribution to aerosols aging. ~~–~~The photochemical mechanism of atmospheric COM and the effect of photo-degradation on its photochemical reactivity are not fully understood. Here, we report ~~To address this knowledge gap,~~ the characteristics of COM photo-degradation ~~and~~, the potential effects of COM photolysis on the photochemical reactivity, and the contribution of COM to reactive oxygen species (ROS) ~~are illustrated~~. COM are identified by excitation-emission matrices combined with parallel factor analysis. We confirm that both water-soluble and water-insoluble COM are photo-bleached, and an average 70% of fluorescence intensities are lost after 7 days of light exposure. ~~Furtherly~~Furthermore, ~~it is found that~~ there is a transformation ~~process of~~from low oxidation to high oxidation HULIS~~.~~ and ~~We propose that the h~~high oxidation HULIS could be used to trace the ~~aging~~ degree of aerosols aging. In terms of photochemical reactivity, compared with before photolysis, the triplet state COM (^{3}COM*) decrease slightly in ambient particulate~~e~~ matter (ambient PM) samples ~~and~~, but increase in primary organic aerosol (POA). ~~However, the~~ ~~COM induce fewer singlet oxygen after photolysis. The photolysis and conversion of COM are the major cause of the change of photochemical activity.~~ The result also ~~enunciate~~ highlight that the photochemical ~~reaction~~ mechanisms and aerosol aging processes are relatively different in various aerosols. Photolysis and conversion of COM reduce photochemical activity, so that COM induce less singlet oxygen. In conclusion, ~~we demonstrated that~~ ~~the~~ photo-degradation of COM not only change the chemical compositions, but also change the roles of the COM in ~~the~~ aerosol aging ~~process~~.

Key word: atmospheric chromophores; photo-degradation; EEMs; triplet state; reactive oxygen species.

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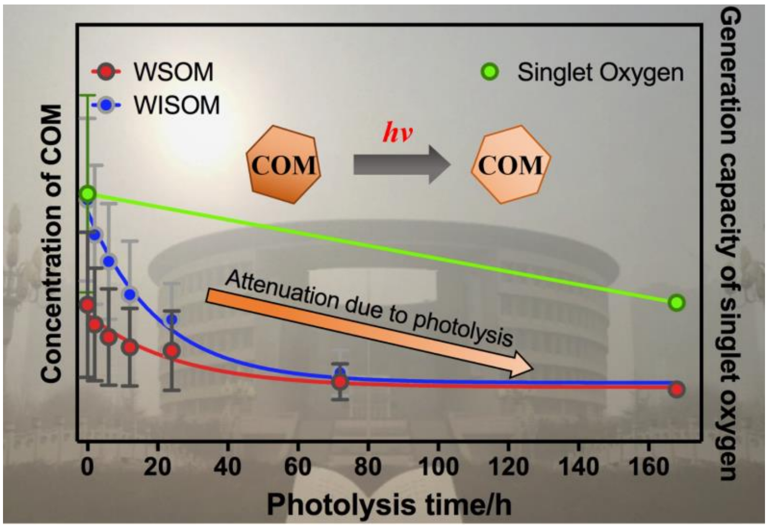
24 
WSOM
WISOM
Singlet Oxygen
COM
hv
COM
Attenuation due to photolysis
Concentration of COM
Generation capacity of singlet oxygen
0
20
40
60
80
100
120
140
160
Photolysis time/h

25

1. Introduction

Chromophoric organic matter~~s~~ (COM) widely exists in the atmospheric environment. COM are mainly derived from biomass combustion emissions and secondary chemistry reactions (Andreae and Gelencser, 2006; Graber and Rudich, 2005; Zappoli et al., 1999). Because of the significant absorption for short wave radiation (the range of near-ultraviolet light to visible light) (Rosario-Ortiz and Canonica, 2016; Cheng et al., 2016), COM may ~~have a significant effect on the atmospheric composition through~~ photoly~~sis~~ze, ~~photo-conversion~~convert components and ~~inducing~~ induce reactive substances (Chen et al., 2018; Wenk et al., 2011; Maizel et al., 2017). Therefore, ~~Simulation~~ simulation and evaluation of COM photochemistry is ~~improve~~ necessary for understanding ~~the mechanism of the~~ aerosol aging.

As photosensitive substances in aerosol, the physical and chemical characteristics of COM change significantly under sunlight exposure (Kieber et al., 2012; Lee et al., 2013; McKnight et al., 2001; Murphy et al., 2013; Cory and McKnight, 2005; Korak et al., 2014; Chin et al., 1994). The specific impacts are summarized. (1) Changes in optical characteristics. Sunlight exposure ~~can~~ cause the photo-bleaching of COM. Previous studies ~~shown~~ reported that chromophores produced by wood-burning were significantly photo-bleached in aerosols (Lee et al., 2014; Zhong and Jang, 2014). Murphy et al. reported that fluorescence intensity of chromophores decreased after 20 h of simulated solar irradiation (Murphy et al., 2018). Yet the mechanisms of photo-bleaching process are still not complete clear. (2) Changes in chemical composition. Photochemistry has~~ve~~ a significant effect on the composition of COM~~,~~. ~~because p~~Photolysis can cause that COM decompose into small molecules~~. Therefore,~~ and COM may have lower volatility and higher oxidation degree after photolysis (Vodacek et al., 1997; Del Vecchio and Blough, 2002; Gonsior et al., 2009; Grieshop et al., 2009). In contrast, COM could also be generated due to photochemical reaction. For example, oligomeric COM could be generated by a mixture of anthracene and naphthalene suspensions ~~due to~~ through self-oxidation under light conditions; photo-oxidation of aromatic isoprene oxides are an important source of high-molecular-weight COM (Altieri et al., 2006; Altieri et al., 2008; Haynes et al., 2019; Holmes and Petrucci, 2006; Perri et al., 2009). COM could also be generated after light exposure (Harrison et al., 2020). Changes in chemical composition affect photochemical activity in turn. Therefore, it is crucial to illustrate the changes in optical characteristics and chemical composition, which could promote understanding the characteristic and mechanisms of COM photochemistry in aerosols.

Atmospheric COM not only decompose and transform, but also participate in the complex photochemical reaction, which further affect the aerosol aging (Malley et al., 2017). On the one hand, COM could participate in atmospheric photochemical processes directly. For example, excited COM react with organic matter~~s~~ and ~~promote~~ generate secondary organic aerosols (Zhao et al., 2015; Saleh et al., 2013; Zhong and Jang, 2014; Lee et al., 2014; Liu et al., 2016). Various secondary photochemi~~cal processes~~stry also increase the complexity of COM composition (Wenk et al., 2011; Zhou et al., 2019; Smith et al., 2014; Richards-Henderson et al., 2015; Kaur and

Anastasio, 2018; Chen et al., 2016a and b). On the other hand, COM also participate in atmospheric photochemical reactions indirectly~~ because COM can~~ through inducinge reactive species. ~~a~~Aromatic ketones could be excited to generate triplet state (^{3}COM*) under light conditions (Rosario-Ortiz and Canonica, 2016; Del Vecchio and Blough, 2004; Wenk et al., 2013; Ma et al., 2010). ^{3}COM* induce reactive oxygen species (ROS), such as singlet oxygen ($^1O_2$), super-oxygen ($•O_2^-$) and hydroxyl (•OH), which could drive aerosol aging (Paul Hansard et al., 2010; Szymczak and Waite, 1988; Zhang et al., 2014; Rosario-Ortiz and Canonica, 2016; Sharpless, 2012; Haag and Gassman, 1984). Photochemical activity is also universal feature of dissolved organic carbon (DOC). Powers et al. (2015) probed the photochemical activity of the deep ocean refractory ~~dissolved organic carbon (~~DOC~~)~~ through simultaneous measuring the rates of both H_2O_2 and O_2^- photoproduction in~~ the~~ laboratory.~~ Photochemical activity is universal feature of DOC.~~ ~~For example,~~ ~~aromatic ketones could be excited to generate triplet state (^{3}COM*) under light conditions (Rosario-Ortiz and Canonica, 2016; Del Vecchio and Blough, 2004; Wenk et al., 2013; Ma et al., 2010). ^{3}COM* induce reactive oxygen species (ROS), such as singlet oxygen ($^1O_2$), super-oxygen ($•O_2^-$) and hydroxyl (•OH), which could drive aerosol aging (Paul Hansard et al., 2010; Szymczak and Waite, 1988; Zhang et al., 2014; Rosario-Ortiz and Canonica, 2016; Sharpless, 2012; Haag and Gassman, 1984).~~ ~~COM have the potential effects on aerosol aging, so i~~It is necessary to clarify the path and effect of COM driving aerosol aging, but the path and effect are both unclear.~~.~~

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 photo~~degradation~~lysis on ~~the optical properties and photochemical reactivity in aerosols~~aerosol aging, we simulate the ~~photolysis~~ process of COM photolysis and COM inducing ROS ~~of~~in primary organic aerosol (POA) and ambient ~~particle~~ particulate matter (ambient PM) in laboratory. The characteristics of photo-degradation in water-soluble and water-insoluble chromophores are clarified by the approach of excitation-emission matrices (EEM) combined with parallel factor analysis (PARAFAC). The effects of ~~aerosol aging~~COM on photochemical reactivity and aerosol aging (photochemical reactivity is characterized by triplet state and singlet oxygen generation capacity) are also stated by the method of reactive species capture technology and electron paramagnetic resonance spectrometer (EPR).

2. Experimental Section

2.1 Sample Collection

A total of 16 samples were collected (The details of the samples are shown in Table S1 of SI). The ambient PM samples were collected in Shaanxi University of Science and Technology, Xi'an, Shaanxi Province (N34°22′35.07″, E108°58′34.58″; the sampling device is about 30 m from the ground). The ambient PM samples were collected on~~ a~~ quartz fiber filter (Pall life sciences, Pall Corporation, America) by an intelligent large-flow sampler (Xintuo XT-1025, Shanghai, China) with a sampling time of 23 h 30 min and a sampling flow rate of 1000 L/min. The ambient PM samples were stored in the refrigerator at -20 °C prior to use.

The POA samples were collected through a combustion chamber. 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. As shown in **Fig.1**, Wheat straw, corn straw, rice straw and wood were burned in the annular combustion chamber when temperatures rose to~~at about~~ 500 °C~~ in the tube stove~~. The clean air was introduced at a flow rate of 2 L/min to ensure complete combustion. The particle matter~~s~~ entered the ~~collected chamber~~mixing box. The clean air was introduced into~~ the collected chamber~~ mixing box at a flow rate of 2 m^3/h to dilute the combustion gas. POA samples were collected on the quartz~~ fiber~~ filter (Pall life sciences, Pall Corporation, America) with a diameter of 37 mm. The POA sample were stored in the refrigerator at -20 °C prior to use.

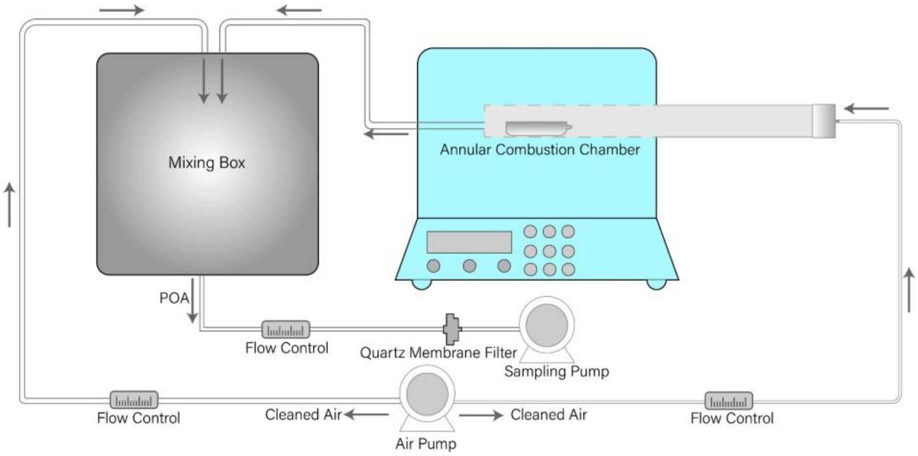


Fig.1 Schematic diagrams of combustion equipment for POA.

2.2 Photolysis experiment

~~A~~The material of reactor is ~~high-purity~~ quartz~~ reactor~~ (**Fig.2a**)~~ was designed for~~ and the reactor was designed for ~~the~~ photolysis experiment~~ (**Fig.1a**)~~. ~~A rubber gasket was embedded on the upper edge of the reactor.~~ The reactor was sealed through clamping~~ed with~~ a~~ high-purity~~ quartz cover to ~~form a sealed environment~~reactor. Two air vents was used to air exchange and Two water cycle 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. The reactor was placed on a magnetic stirrer and the rotation speed was 200 rmp to stabilize the temperature and humidity (~50%). 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 S1 of SI). The light intensity per unit area was about 1.2-1.3 times the solar light at 12:00, at N34°22′35.07″, E108°58′34.58″. A small storage platform ~~support~~ was placed in the reactor ~~and the samples were placed on the support~~to place quartz reaction cell (**Fig.2b**) and quartz plate (**Fig.2c**). The illumination times were 0 h, 2 h, 6 h, 12 h, 24 h, 3 d and 7 d, respectively.

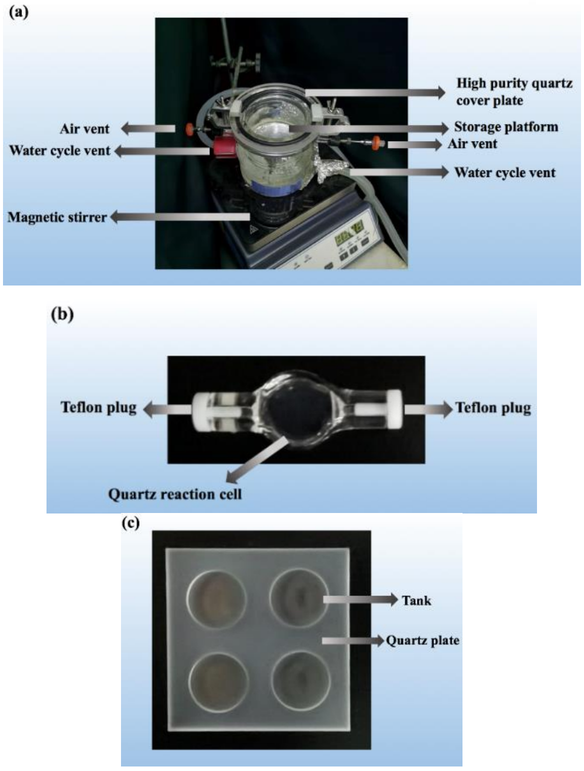


Fig.~~1~~ 2 Schematic diagrams of the photochemical devices. (a) The reactor is used for maintaining the reaction environment.~~ The water cycle vents are connected with a water circulator to maintain the temperature.~~ (b) The reactor is used for triplet state experiments. The reactor is made of quartz. The plugs are made of Teflon. The internal volume is 200 µL. (c) A reactor 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.

2.3 Sample extraction

The samples extracts were obtained by the approach of ultrasonic extraction. The original and photolyzed samples were extracted with ultra-pure water (>18.2 MΩ•cm, Master series, Hitech, China) and the suspensions were filtered through a 0.45 µm filter (Jinteng, China) to obtain the water-soluble organic matter (WSOM). After water extraction, the samples were further extracted with methanol (HPLC Grade, Fisher Chemical, America) to obtain water-insoluble organic matter (WISOM) using the above method. The blank samples were also extracted. The~~ specific~~ blank extraction method was the same as sample extraction, which was used to correct the effect of the background.

2.4 OC/EC analysis

The method of organic carbon (OC) analysis could refer to the previous literature (Mu et al., 2019). Briefly, 100 µL of extracts were injected on the clean quartz filter. Then, the filters were dried out~~ with~~ by a rotary evaporator. Carbonaceous components were analyzed by the OC/EC online analyzer (Model 4, Sunset, America) with the approach of NIOSH 870 protocol (Karanasiou et al., 2015). Six parallel samples were analyzed and~~ the results showed that~~ the uncertainty of the method was <3.7% (one standard deviation).

2.5 Optical analysis

The light absorption and EEM spectra of the extracts were ~~analyzed~~ measured by an Aqualog fluorescence spectrophotometer (Horiba Scientific, America). The extracts were diluted for optical analysis (The concentrations and dilution factors are shown in Table S2 of SI). 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~~ emission wavelength was 250-800 nm. The interval was 5 nm. The exposure time was 0.5 s. Water and methanol~~The~~ background samples were ~~also~~ measured~~analyzed~~ using the same method and the background signals were subtracted from the sample signals.

The EEM data was analyzed by the PARAFAC model to identify ~~chromophores~~ fluorophores (The detailed analysis process refers to the previous papers) (Chen et al., 2016b; Chen et al., 2016a). 111 samples were used to create the model. WSOM and WISOM were combined in the dataset to create the PARAFC model. Briefly, according to the EEM characteristics and the residual error variation trend of the 2-7 component PARAFAC models, 4 component PARAFAC model was selected (Analysis error of the models are shown in Figure S2 of SI).

2.6 Triplet state generation experiment

The triplet states generation ability before and after photolysis were studied. Chemical probe 2,4,6-trimethylphenol (TMP) was used as the capturing agent for the triplet state. 60 μL of WSOM extracts (OC concentrations are shown in Table S3) and 60 μL of TMP solution (c_{TMP} = 20 μM, Aladdin, China) were mixed in the cell (**Fig.~~1b~~2b**). The cell was placed in the reactor (**Fig.~~1a~~2a**) and the reaction conditions were the same as shown in 2.2. The illumination times was 0, 5, 10, 15, 30, 45, 60 and 90 min, respectively. 90 μL mixed solution was taken out from the cell at different time points. Then 30 μL of phenol solution (c_{phenol} = 50 μM, Aladdin, China) were added into the mixed solution (Phenol solution was used as the internal standard substance for TMP quantification). TMP was quantified by liquid chromatography (LC).

The analyzed parameters of LC are as follows: C18 column (Xuanmei, China); mobile phase: acetonitrile/water = 1/1 (v/v); flow rate: 1 mL/min; UV detector: detection wavelength 210 nm. The retention time is 14.5 min. Kaur and Anastasio (2018) and Richards-Henderson et al. (2015) have ~~found~~ reported that TMP consumption conform to first-order kinetics in the triplet state capture reaction. The first-order kinetic equation was used to fit exponential relationship among the TMP concentration (c_{TMP}/μM), the illumination time (t/min) and triplet state generation rate constants (k_{TMP}/min^{-1}):

$$c_{TMP} = a \cdot e^{-t\times k_{\mathrm{TMP}}\cancel{\times t}} \qquad (1)$$

2.7 Triplet state driving singlet oxygen experiment

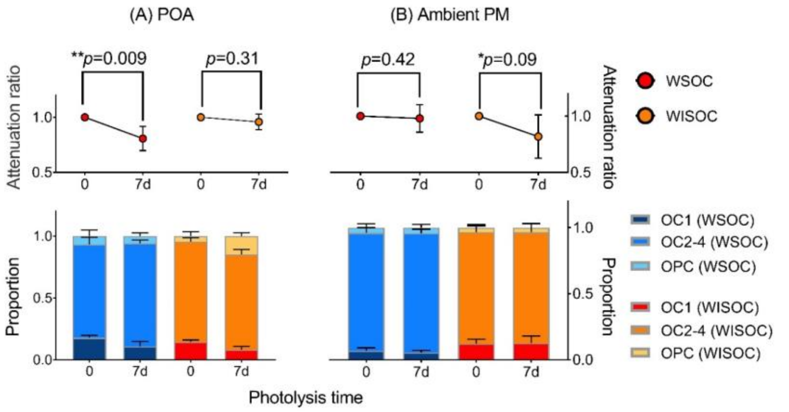
The effects of the COM photolysis on singlet oxygen ~~in aerosols~~ were studied. 4-Hydroxy-2, 2, 6, 6-tetramethylpiperidine (TEMP, c_{TEMP}=240 mM, Aladdin, China) was used as the capturing agent of singlet oxygen and captured singlet oxygen was quantified by EPR spectrometer (MS5000, Freiberg, Germany). Sorbic acid (SA, C_{SA}=133.3 μM, Aladdin, China) was used as quenching agent for triplet state. The method was as follows: (1) 40 μL WSOM, 40 μL TEMP and 40 μL ultra-pure water were mixed in the tanks (**Fig.~~1c~~2c**). The mixed solution was placed in the reactor (**Fig.~~1a~~2a**). Then, 50 μL of the mixed solution was taken out by capillary for EPR analysis; (2) 40 μL of WSOM, 40 μL of TEMP and 40 μL of ultra-pure water were mixed. The mixed solution was placed in the reactor for 60 min without illumination. Then 50 μL of the mixed solution was taken out by capillary for EPR analysis; (3) 40 μL of WSOM, 40 μL of TEMP and 40 μL of ultra-pure water were mixed in the cell. The mixed solution was placed in the reactor for 60 min with illumination. 50 μL of the mixed solution was taken out by capillary for EPR analysis; (4) 40 μL of WSOM, 40 μL of TEMP and 40 μL of SA solution were mixed in the cell. The mixed solution was placed in the reactor for 60 min with illumination, then 50 μL of the mixed solution was taken out by capillary for EPR analysis.

3. Results and discussion

3.1 Effect of COM photo-degradation on carbonaceous components

Organic matter~~s~~ can be decomposed and transformed in aerosol due to illumination (Wong et al., 2015). **Fig.~~2~~ 3** describe the variable characteristics of total organic carbon and carbonaceous components before and after COM photolysis. The results show that both water-soluble and water-insoluble organic matter undergo partial~~ly~~ photolysis in POA samples (**Fig.~~2A~~3A**), with an average decrease of 22.1% and 3.5%, respectively.~~ Compared with POA, ~~ WISOC decompose obviously in ambient PM than in POA, with an average decrease of 26.3%, while the WSOC do not change significantly in ambient PM (**Fig.~~2B~~3B**).

Photolysis also results in the variation on carbonaceous components. In POA~~ samples~~ (**Fig.~~2A~~3A**), the relative content of the OC1 (OC1 and OC2-4 are the different stage in the process of thermal-optical analysis) decrease, which is the main loss of OC. The organic matter~~s~~ in the OC1 stage are characterized by small molecular weight and highly volatile (Karanasiou et al., 2015). The result shows that OC1 has a stronger ability of photo-decompose. On the other hand, the pyrolysis carbon (OPC) in WISOM show an increasing trend (an average increase of 2.4 times). Generally, the pyrolysis carbon is oxygen-containing substance. Thus, the increase of oxygen-containing organics may be due to the aerosols aging. In ~~Contrast ~~contrast ~~with ~~to POA, the carbonaceous components are relatively stable in ambient PM (**Fig.~~2B~~3B**). The result reflects that ambient PM samples have been subjected to sufficient atmospheric oxidation, so organic matter~~s~~ are not decomposed or oxidized again.



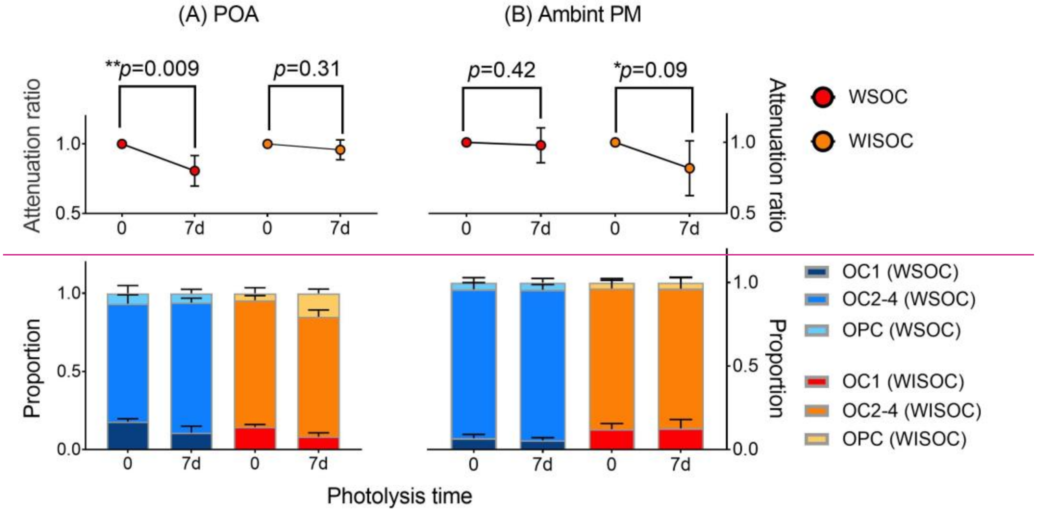
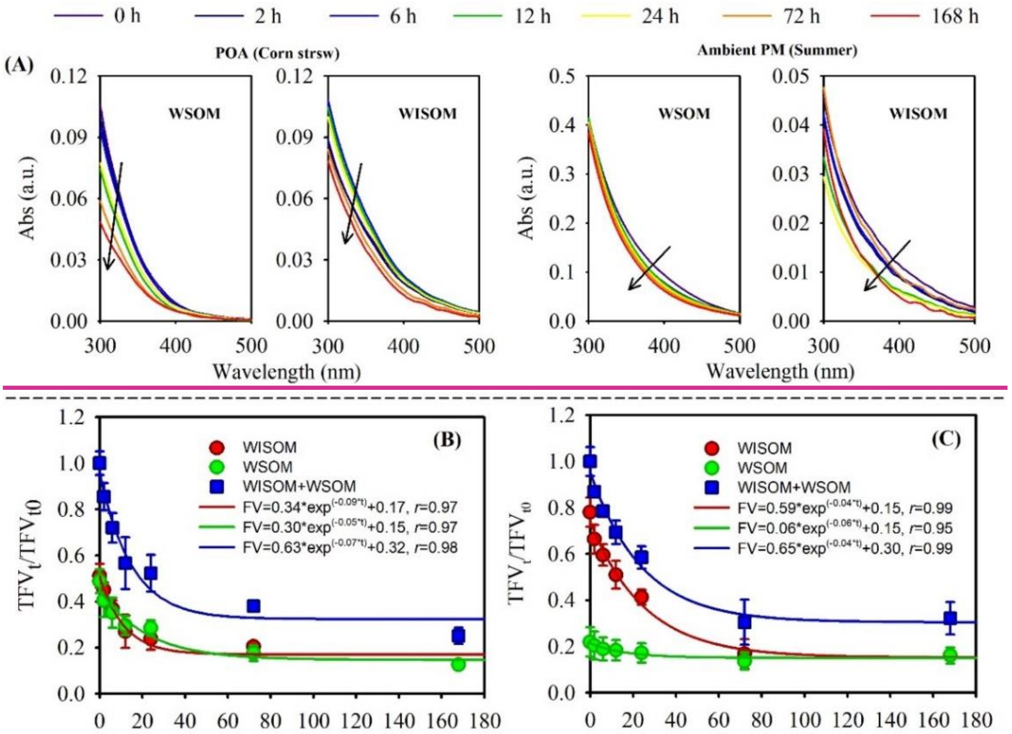


Fig.~~2~~ 3 Variations of total carbon and carbonaceous components before and after photolysis. The *p*-value is the probability that two sets of data have the same level (two-tailed test). * and ** are represent the significant difference at the 0.1 and 0.01 levels, respectively.

3.2 Effect of COM photo-degradation on optical properties

Both absorbance and total fluorescence volume (TFV, RU-nm2/m3)~~ represent an~~ ~~obvious~~ significantly decreas~~ing~~e~~ trend~~ d~~ue to~~uring aerosol photolysis (Fig.~~3~~4). Changes in optical properties are shown in Figure S3, S4 and S5. The decrease of absorbance confirm that COM are photo-bleached (Duarte et al., 2005~~).~~) and ~~The~~ the ~~subduction~~ decay function of photolysis on absorbance is significant (Aiona et al., 2018). 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. 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. ~~–~~In POA (**Fig.~~3B~~4B**), TFV decrease by 74.8% on average and the attenuation characteristics of water-soluble and water-insoluble components are similar.

However, ~~The~~ the attenuation of fluorescence intensities is different from Aiona's paper (Aiona et al., 2018). The photolysis ~~–~~ability of COM is various and ~~Changes~~ changes in fluorescence intensities may depend on the types of COM and the photochemical environment. Exceptionally, the water-insoluble component of wood burning only decrease by 9.0% (Figure S5), which is significantly different from other POA samples. The attenuation ~~characteristics~~ of TFV and WISOC ~~of~~ ~~wood burning~~ (section 3.1) are similar in wood burning samples, which probably attribute to the slight generation of secondary water-insoluble organic substances. The characteristics of TFV attenuation in ambient PM (rate constant $k = 0.04$ h^{-1}) is different from POA ($k = 0.07$ h^{-1}). Compared with water-soluble chromophores, the water-insoluble chromophores photo-decompose obviously and the TFV decrease by 79.1%~~. In contrast, changes in the~~, but water-soluble chromophores ~~are~~ only 21.9% on average~~, while 48.8% in POA samples~~. The results suggest that ~~The low attenuation result from~~ COM have undergone a long-term atmospheric aging ~~process~~ ~~–~~and ~~the~~ water-soluble COM ~~are~~ have ~~easier~~ greater ability to be ~~photolysis~~photolyzed.



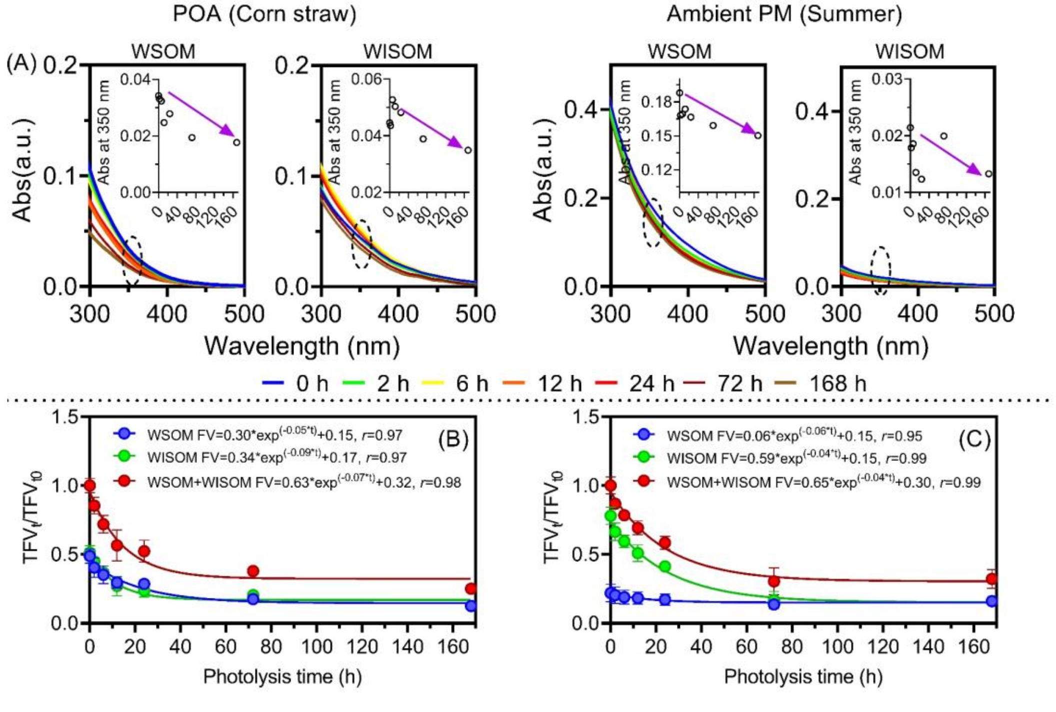
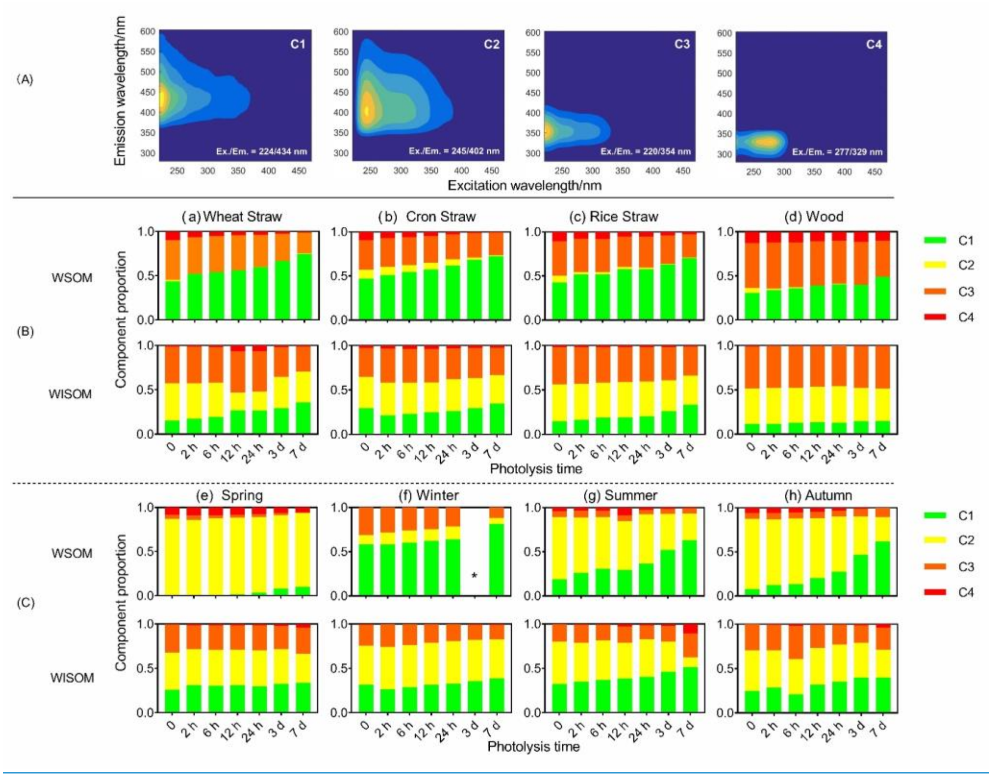


Fig.~~3~~ 4 The changes of light absorption and fluorescence volume ~~in~~ during the photolysis process. (A) The light absorption spectrum. The scatter plot is changes in Abs at 350 nm. ~~–~~(B) and (C) show the attenuation curve of average fluorescence volume of POA (except for the wood sample) and ambient PM samples, respectively.

Four types of COM are identified by the approach of EEMs-PARAFAC and the composition variations are studied (Fig.~~4A~~5A). 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 of chromophores in WSOM and WISOM. The fluorescence peaks of C1 and C2 appear at (Ex./Em. = 224/434 nm) and (Ex./Em. = 245/402 nm), and the peaks~~characteristics~~ are similar to high and low oxidation HULIS, respectively (Chen et al., 2016b; Birdwell and Engel, 2010). The peaks of C3 and C4 appear at (Ex./Em. = 220/354 nm) and (Ex./Em. = 277/329 nm) and these two ~~chromophores~~ fluorophores were ~~identified~~ associated ~~as~~ with protein-like organic matter~~s~~ (PLOM-1 and PLOM-2) in previous studies (Sierra et al., 2005; Huguet et al., 2009; Chen et al., 2016a and 2016b; Coble, 2007; Fellman et al., 2009).

The compositions of chromophores change significantly ~~in the~~during photolysis process. In POA (**Fig.~~4B~~5B**), the high-oxidation HULIS ~~show an obvious~~ increas~~ing trend~~e significantly in water-soluble component and the relative content increase by 25.7% on average. On the contrary, low oxidation HULIS and PLOM ~~show a~~ decreas~~ing trend~~e ~~and the relative attenuation are~~ by 6.0% and 19.7%, respectively. The proportion variation indicates that high-oxidation HULIS chromophores could be generated ~~in the photochemistry process~~ and low oxidation HULIS and PLOM chromophores may be photolyzed (Tang et al., 2020; Chen et al., 2020). Not only in water-soluble chromophores, the content of high-oxidation HULIS also increase in water-insoluble chromophores (average 17.5~~%).~~%) and ~~Low~~low-oxidation HULIS also decrease in water-insoluble chromophores. In ambient PM, the content of high-oxidation HULIS increase and the low-oxidation HULIS decrease (**Fig.~~4C~~5C**), which reveal that low-oxidation HULIS could be transformed into high-oxidation HULIS ~~in aerosol aging process~~ (Chen et al., 2016a). Thus, high-oxidation HULIS could be used to trace the degree of aerosols aging ~~degree~~.



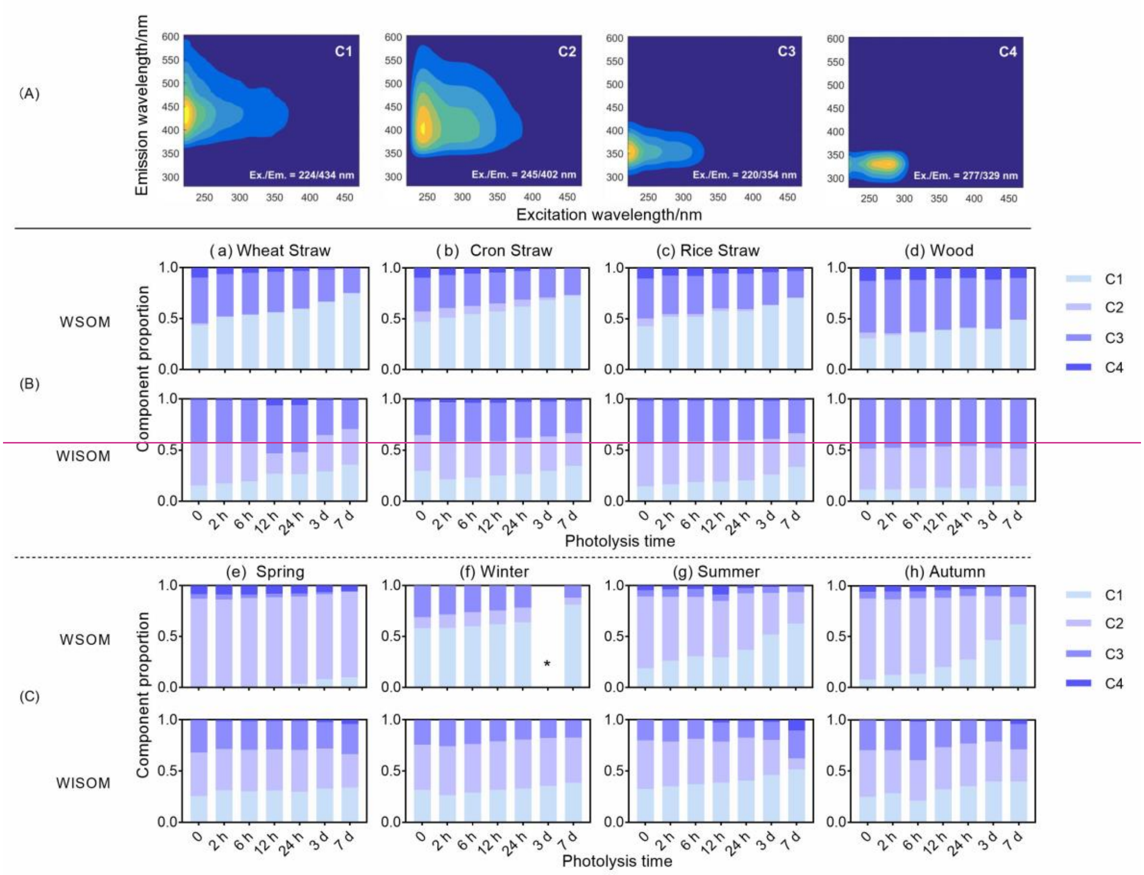


Fig.~~4~~ 5 (A) The EEM spectra of chromophores; (B) is the variation characteristics of chromophores in POA; (C) is the variation characteristics of chromophores in ambient PM. *: The data of 3-day photolysis of water-soluble chromophores in winter is unavailable.

3.3 Effect of COM photo-degradation on aerosol photochemical reactivity

COM photo-degradation has a significant effect on aerosol photochemical reactivity. The photochemical activity is characterized by the generating ability of ~~triplet state~~ ^{3}COM* and singlet oxygen. **Fig.~~5~~ 6** show the difference of triplet state generation capability before and after the photolysis (Details are shown in Figure S6 of SI). In ambient PM, ~~The~~ the generation rate of triplet state is decreased by 11% on average after ~~COM~~ COM photolysis ~~in ambient PM~~, while statistical analysis shows that photo-degradation does not significantly affect the triplet state generation (p = 0.38, two-tailed test). On the contrary, the triplet states generation rate markedly increases by 75% on average in POA (p = 0.07, two-tailed test), which indicate that ~~COM~~ photo-degradation ~~has a~~ significantly ~~improvement effect on~~ promote triplet state generation. COM are photo-decomposed, while the triplet state generation ability remains unchanged or increase. The results are not as expected. However, the result can be explained by recent study (Chen et al. 2020 for ACPD): only a small number of chromophores have the ability to generate triplet states in aerosols. The decomposition of most chromophores do not represent the decomposition of these specific types of chromophores. We use a high concentration of TMP, in this case, TMP mainly capture short-lived triplet state (Rosado-Lausell et al., 2013). Thus, chromophores that can form a short-lived triplet state ~~–~~ may not be reduced or even generated during the photolysis process.

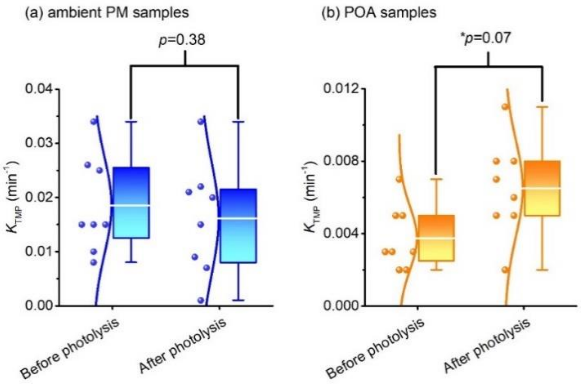


Fig.~~5~~ 6 The changes of the triplet state generation capacity in (a) ~~the~~ ambient PM and (b) POA samples before and after photolysis. The line from bottom to top in the box plots are minimum, first quartile, the average value (white lines), third quartile, and maximum, respectively. The p-value is the probability that two sets of data have the same level (two-tailed test). * represents a significant difference at the 0.1 level.

COM can generate triplet states and furtherly induce singlet oxygen (McNeill and Canonica, 2016). The effects of COM photo-degradation on singlet oxygen are illustrated ~~through the approach of~~ using chemical capture and EPR analysis. Typical EPR~~s~~ spectra of $^1O_2$ are shown in **Fig.~~6~~ 7** (EPR spectra of all samples are shown in Figure S7 and Figure S8). More narrowly, in the original POA samples (i.e., the sample with photolysis time is 0, details of samples are described in section 2.2), there is no significant $^1O_2$ signal before light excitation (the red curve in **Fig.~~6A~~ 7A (I)**) and only a small amount of $^1O_2$ is generated after 60 min in dark (the red curve in **Fig.~~6A~~ 7A (II)**), which indicated that POA has certain oxidability. As expected, compared with the samples without light excitation (the red curve in **Fig. ~~6A~~ 7A (I)**), the signal intensity of $^1O_2$ increases by a factor of 3 ~~times~~ after 60 minutes of light excitation (the red curve in **Fig. ~~6A~~ 7A (III)**), which prove the significant promoting effect of light on $^1O_2$. However, $^1O_2$ is not reduced when the triplet state is quenched by sorbic acid (the red curve in **Fig.~~6A~~ 7A (IV)**). Sorbic acid is a trapping agent of high-energy triplet state (triplet energies E_T = 239-247 kJ/mol) (Zhou et al., 2019; Moor et al., 2019), therefore, the above results indicate that the low-energy ^{3}COM* (E_T <239 kJ/mol) may be the main precursor for $^1O_2$ (E_T = 94 kJ/mol) in POA.

The COM photo-degradation can change the yield of $^1O_2$. Compared with original POA samples, the signal intensity of $^1O_2$ decreases significantly in the samples with 7 days of photolysis (the blue curve in **Fig.~~6A~~7A**), with an average decrease of 42.1% (**Fig.~~6C~~7C**), which prove that photo-degradation has a attenuating~~restraining~~ effect on the photochemical activity~~ in POA~~. Similar to the original sample, in the photolyzed samples, the signal intensity of $^1O_2$ does not decrease obviously when the high-energy triplet states are quenched by sorbic acid~~ in the photolyzed samples~~. The mechanism is the same as the original samples. The results also reveal that~~ the~~ COM photo-degradation~~ process~~ do not change the mechanism of low-energy ^{3}COM* inducing $^1O_2$ in POA.

The photochemical characteristics of ambient PM are different from POA. More narrowly, there is no obvious $^1O_2$ signal in original ambient PM samples before light excitation (the red curve in **Fig.~~6B~~ 7B (I)**). $^1O_2$ is also not generated after 60 min in dark (the red curve in **Fig.~~6B~~ 7B (II)**). The content of $^1O_2$ increase significantly after 60 minutes of light excitation (the red curve in **Fig.~~6B~~ 7B (III)**). When the triplet states are quenched by sorbic acid (**Fig.~~6B~~7B (IV)**), the signal of $^1O_2$ disappears. The result suggests that $^1O_2$ is mainly induced by high-energy ^{3}COM* in ambient PM. Compared with the original samples, the signal intensity of $^1O_2$ decrease by 41.0% on average in photolyzed samples (the red curve in **Fig.6B**). This characteristic ~~reveal~~ suggests the~~ restraining~~ attenuating effect of COM photo-degradation on photochemical activity in ambient PM~~. The restraining effect~~, which is similar to POA. However, the quenching effect of sorbic acid on various aerosols are different (**Fig.~~6~~ 7 (IV)**). The above results directly ~~prove~~ show that the precursor of high-energy triplet states could be photolyzed, which directly lead to the decrease of $^1O_2$ yield in the ambient PM. Other experiments are needed to~~ prove~~ study whether the low-energy triplet precursors in POA are photolyzed and cause a decrease in the yield of $^1O_2$.

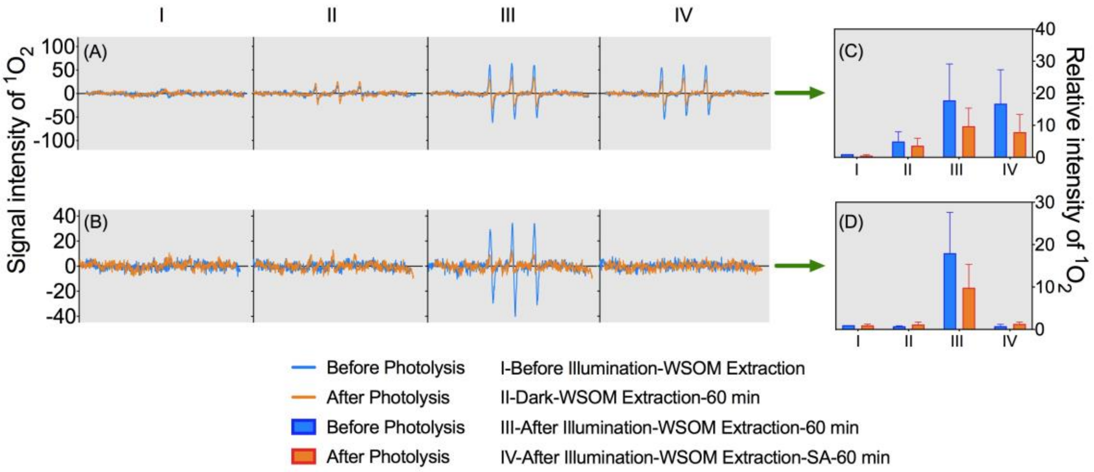


Fig.~~6~~ 7 Variations of DOM inducing $^1O_2$ before and after photolysis. (A) and (C) are the results obtained from POA samples. (B) and (D) are the results obtained from Ambient PM. The left of the figure was the EPR spectra of $^1O_2$. The right of the figure was the content variations of $^1O_2$. Relative content was calculated with a standard of the signal intensity of $^1O_2$. The standard is the signal intensity of $^1O_2$, which is induced by un-photolyzed and un-illuminated samples.

4. Implication

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. 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~~e characteristics of COM photo-degradation and the~~ effects of COM photo-degradation on the photochemical activity in~~ different~~ aerosols are studied. ~~Firstly, we prove that the photo-degradation could lead to COM decompose and change in types. The conversion process of low-oxidation HULIS to high-oxidation HULIS is observed in ambient PM, which reflect 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 are also effected by COM photo-degradation. Secondly, w~~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. Triplet state generation ability remain unchanged in ambient PM ~~or~~ and increased~~in the~~ in POA during aerosol aging~~process,~~. On the one hand, only a small amount of chromophore could generate ^{3}COM* in aerosols. Thus, COM photo-degradation could not properly illustrate changes in ^{3}COM*. On the other hand, the energy of capturing agents was closely related to measured ^{3}COM* 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. ~~while p~~Photo-degradation has a significant attenuating~~restraining~~ effect on the $^1O_2$ yield. ~~So~~ 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 ^{3}COM* 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.

Data availability. All data that support the findings of this study are available in this article and its Supplement or from the corresponding author on request.

Supporting information. Additional details, including Tables S1−~~S3~~S5, Figures S1−S8, calculation of optical characteristics of WSOM/WISOM, are contained in the SI.

Author contributions. QC and ZM designed the experiments and data analysis. ZM and LZ performed sample collection. ZM performed the photochemical experiment. ZM and DG performed the OC/EC analysis and optical analysis. HL performed the EPR analysis. QC prepared the paper with the contributions from all co-authors.

Competing interests. The authors declare that they have no conflict of interest.

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References

Aiona, P. K., Luek, J. L., Timko, S. A., Powers, L. C., Gonsior, M., and Nizkorodov, S. A.: Effect of Photolysis on Absorption and Fluorescence Spectra of Light-Absorbing Secondary Organic Aerosols, ACS Earth Space Chem., 2, 235-245, 10.1021/acsearthspacechem.7b00153, 2018.

Alfarra, M. R., Prevot, A. S., Szidat, S., Sandradewi, J., Weimer, S., Lanz, V. A., Schreiber, D., Mohr, M., and Baltensperger, U.: Identification of the mass spectral signature of organic aerosols from wood burning emissions, Environ. Sci. Technol., 41, 5770-5777, http://dx.doi.org/10.1021/es062289b, 2007.

Altieri, K. E., Carlton, A. G., Lim, H. J., Turpin, B. J., and Seitzinger, S. P.: Evidence for oligomer formation in clouds: Reactions of isoprene oxidation products, Environ. Sci. Technol., 40, 4956-4960, http://dx.doi.org/10.1021/es052170n, 2006.

Altieri, K. E., Seitzinger, S. P., Carlton, A. G., Turpin, B. J., Klein, G. C., and Marshall, A. G.: Oligomers formed through in-cloud methylglyoxal reactions: Chemical composition, properties, and mechanisms investigated by ultra-high resolution FT-ICR mass spectrometry, Atmos. Environ., 42, 1476-1490, http://dx.doi.org/10.1016/j.atmosenv.2007.11.015, 2008.

Andreae, M. O., and Gelencser, A.: Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols, Atmos. Chem. Phys., 6, 3131-3148, http://dx.doi.org/10.5194/acp-6-3131-2006, 2006.

Birdwell, J. E., and Engel, A. S.: Characterization of dissolved organic matter in cave and spring waters using UV−Vis absorbance andfluorescence spectroscopy, Org. Geochem., 41, http://dx.doi.org/10.1016/j.orggeochem.2009.11.002, 2010.

Chen, Q., Miyazaki, Y., Kawamura, K., Matsumoto, K., Coburn, S., Volkamer, R., Iwamoto, Y., Kagami, S., Deng, Y., Ogawa, S., Ramasamy, S., Kato, S., Ida, A., Kajii, Y., and Mochida, M.: Characterization of Chromophoric Water-Soluble Organic Matter in Urban, Forest, and Marine Aerosols by HR-ToF-AMS Analysis and Excitation-Emission Matrix Spectroscopy, Environ. Sci. Technol., 50, 10351-10360, http://dx.doi.org/10.1021/acs.est.6b01643, 2016a.

Chen, Q., Mu, Z., Xu, L., Wang, M., Wang, J., Shan, M., Yang, X., Fan, X., Song, J., Wang, Y., Lin, P., Zhang, L., Shen, Z., and Du, L.: Triplet State Formation of Chromophoric Dissolved Organic Matter in Atmospheric Aerosols: Characteristics and Implications, Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-1032, 2020.

Chen, Q., Li, J., Hua, X., Jiang, X., Mu, Z., Wang, M., Wang, J., Shan, M., Yang, X., Fan, X., Song, J., Wang, Y., Guan, D., and Du, L.: Identification of species and sources of atmospheric chromophores by fluorescence excitation-emission matrix with parallel factor analysis, Sci. Total Environ., 718, 137322, http://dx.doi.org/10.1016/j.scitotenv.2020.137322, 2020.

Chen, Q. C., Ikemori, F., and Mochida, M.: Light Absorption and Excitation-Emission Fluorescence of Urban Organic Aerosol Components and Their Relationship to Chemical Structure, Environ. Sci. Technol., 50, 10859-10868, http://dx.doi.org/10.1021/acs.est.6b02541, 2016b.

Chen, Y., Zhang, X., and Feng, S.: Contribution of the Excited Triplet State of Humic Acid and Superoxide Radical Anion to Generation and Elimination of Phenoxyl Radical, Environ. Sci. Technol., 52, 8283-8291, http://dx.doi.org/10.1021/acs.est.8b00890, 2018.

Cheng, Y., He, K. B., Du, Z. Y., Engling, G., Liu, J. M., Ma, Y. L., Zheng, M., and Weber, R. J.: The characteristics of brown carbon aerosol during winter in Beijing, Atmos. Environ., 127, 355-364, http://dx.doi.org/10.1016/j.atmosenv.2015.12.035, 2016.

Chin, Y. P., Aiken, G., and O'Loughlin, E.: Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances, Environ. Sci. Technol., 28, 1853-1858, http://dx.doi.org/10.1021/es00060a015, 1994.

Chow, J. C., Watson, J. G., Chen, L. W., Arnott, W. P., Moosmuller, H., and Fung, K.: Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols, Environ. Sci. Technol., 38, 4414-4422, http://dx.doi.org/10.1021/es034936u, 2004.

Chu, C. H., Lundeen, R. A., Sander, M., and McNeill, K.: Assessing the Indirect Photochemical Transformation of Dissolved Combined Amino Acids through the Use of Systematically Designed Histidine-Containing Oligopeptides, Environ. Sci. Technol., 49, 12798-12807, http://dx.doi.org/10.1021/acs.est.5b03498, 2015.

Coble, P. G.: Marine optical biogeochemistry: the chemistry of ocean color, Chem. Rev., 107, 402-418, http://dx.doi.org/10.1021/cr050350+, 2007.

Cory, R. M., and McKnight, D. M.: Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter, Environ. Sci. Technol., 39, 8142-8149, http://dx.doi.org/10.1021/es0506962, 2005.

Del Vecchio, R., and Blough, N. V.: Photobleaching of chromophoricdissolved organic matter in natural waters: kinetics and modeling, Mar. Chem., 78, 231–253, http://dx.doi.org/10.1016/S0304-4203(02)00036-1, 2002.

Del Vecchio, R., and Blough, N. V.: On the origin of the optical properties of humic substances, Environ. Sci. Technol., 38, 3885-3891, http://dx.doi.org/10.1021/es049912h, 2004.

Duarte, R. M. B. O., Pio, C. A., and Duarte, A. C.: Spectroscopic study of the water-soluble organic matter isolated from atmospheric aerosols collected under different atmospheric conditions, Anal. Chim. Acta, 530, 7-14, http://dx.doi.org/10.1016/j.aca.2004.08.049, 2005.

Fellman, J. B., Miller, M. P., Cory, R. M., D'Amore, D. V., and White, D.: Characterizing Dissolved Organic Matter Using PARAFAC Modeling of Fluorescence Spectroscopy: A Comparison of Two Models, Environ. Sci. Technol., 43, 6228-6234, http://dx.doi.org/10.1021/es900143g, 2009.

Gonsior, M., Peake, B. M., Cooper, W. T., Podgorski, D., D'Andrilli, J., and Cooper, W. J.: Photochemically induced changes in dissolved organic matter identified by ultrahigh resolution fourier transform ion cyclotron resonance mass spectrometry, Environ. Sci. Technol., 43, 698-703, http://dx.doi.org/10.1021/es8022804, 2009.

Graber, E. R., and Rudich, Y.: Atmospheric HULIS: how humic-like are they? A comprehensive and critical review, Atmos. Chem. Phys., 6, 729-753, http://dx.doi.org/10.5194/acp-6-729-2006, 2005.

Grieshop, A. P., Donahue, N. M., and Robinson, A. L.: Laboratory investigation of photochemical oxidation of organic aerosol from wood fires 2: analysis of aerosol mass spectrometer data, Atmos. Chem. Phys., 9, 2227-2240, http://dx.doi.org/DOI 10.5194/acp-9-2227-2009, 2009.

Haag, W. R., and Gassman, E.: Singlet oxygen in surface waters-Part II: Quantum yields of its production by some natural humic materials as a function of wavelength, Chemosphere, 13, 641-650, http://dx.doi.org/10.1016/0045-6535(84)90200-5, 1984.

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., 4, 762-773, http://dx.doi.org/10.1021/acsearthspacechem.0c00061, 2020.

Haynes, J. P., Miller, K. E., and Majestic, B. J.: Investigation into Photoinduced Auto-Oxidation of Polycyclic Aromatic Hydrocarbons Resulting in Brown Carbon Production, Environ. Sci. Technol., 53, 682-691, http://dx.doi.org/10.1021/acs.est.8b05704, 2019.

Holmes, B. J., and Petrucci, G. A.: Water-soluble oligomer formation from acid-catalyzed reactions of levoglucosan in proxies of atmospheric aqueous aerosols, Environ. Sci. Technol., 40, 4983-4989, http://dx.doi.org/10.1021/es060646c, 2006.

Huguet, A., Vacher, L., Relexans, S., Saubusse, S., Froidefond, J. M., and Parlanti, E.: Properties of fluorescent dissolved organic matter inthe Gironde Estuary, Org. Geochem., 40, http://dx.doi.org/10.1016/j.orggeochem.2009.03.002, 2009.

Karanasiou, A., Minguillón, M. C., Viana, M., Alastuey, A., Putaud, J.-P., Maenhaut, W., Panteliadis, P., Močnik, G., Favez, O., and Kuhlbusch, T. A. J.: Thermal-optical analysis for the measurement of elemental carbon (EC) and organic carbon (OC) in ambient air a literature review, Atmos. Meas. Tech. Discuss., 8, 9649-9712, http://dx.doi.org/10.5194/amtd-8-9649-2015, 2015.

Kaur, R., and Anastasio, C.: First Measurements of Organic Triplet Excited States in Atmospheric Waters, Environ. Sci. Technol., 52, 5218-5226, http://dx.doi.org/10.1021/acs.est.7b06699, 2018.

Kieber, R. J., Adams, M. B., Wiley, J. D., Whitehead, R. F., Avery, G. B., Mullaugh, K. M., and Mead, R. N.: Short term temporal variability in the photochemically mediated alteration of chromophoric dissolved organic matter (CDOM) in rainwater, Atmos. Environ., 50, 112-119, http://dx.doi.org/10.1016/j.atmosenv.2011.12.054, 2012.

Korak, J. A., Dotson, A. D., Summers, R. S., and Rosario-Ortiz, F. L.: Critical analysis of commonly used fluorescence metrics to characterize dissolved organic matter, Water Res., 49, 327-338, http://dx.doi.org/10.1016/j.watres.2013.11.025, 2014.

Latch, D. E., and McNeill, K.: Microheterogeneity of singlet oxygen distributions in irradiated humic acid solutions, Science, 311, 1743-1747, http://dx.doi.org/10.1126/science.1121636, 2006.

Lee, H. J., Laskin, A., Laskin, J., and Nizkorodov, S. A.: Excitation-emission spectra and fluorescence quantum yields for fresh and aged biogenic secondary organic aerosols, Environ. Sci. Technol., 47, 5763-5770, http://dx.doi.org/10.1021/es400644c, 2013.

Lee, H. J., Aiona, P. K., Laskin, A., Laskin, J., and Nizkorodov, S. A.: Effect of solar radiation on the optical properties and molecular composition of laboratory proxies of atmospheric brown carbon, Environ. Sci. Technol., 48, 10217-10226, http://dx.doi.org/10.1021/es502515r, 2014.

Liu, J. M., Lin, P., Laskin, A., Laskin, J., Kathmann, S. M., Wise, M., Caylor, R., Imholt, F., Selimovic, V., and Shilling, J. E.: Optical properties and aging of light-absorbing secondary organic aerosol, Atmos. Chem. Phys., 16, 12815-12827, http://dx.doi.org/10.5194/acp-16-12815-2016, 2016.

Ma, J., Del Vecchio, R., Golanoski, K. S., Boyle, E. S., and Blough, N. V.: Optical properties of humic substances and CDOM: effects of borohydride reduction, Environ. Sci. Technol., 44, 5395-5402, http://dx.doi.org/10.1021/es100880q, 2010.

Maizel, A. C., Li, J., and Remucal, C. K.: Relationships Between Dissolved Organic Matter Composition and Photochemistry in Lakes of Diverse Trophic Status, Environ. Sci. Technol., 51, 9624-9632, http://dx.doi.org/10.1021/acs.est.7b01270, 2017.

Malley, P. P. A., Grossman, J. N., and Kahan, T. F.: Effects of Chromophoric Dissolved Organic Matter on Anthracene Photolysis Kinetics in Aqueous Solution and Ice, J. Phys. Chem. A, 121, 7619-7626, http://dx.doi.org/10.1021/acs.jpca.7b05199, 2017.

McKnight, D. M., Boyer, E. W., Westerhoff, P. K., Doran, P. T., Kulbe, T., and Andersen, D. T.: Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity, Limnol. Oceanogr., 46, 38-48, http://dx.doi.org/10.4319/lo.2001.46.1.0038, 2001.

McNeill, K., and Canonica, S.: Triplet state dissolved organic matter in aquatic photochemistry: reaction mechanisms, substrate scope, and photophysical properties, Environ. Sci. Process Impacts, 18, 1381-1399, http://dx.doi.org/10.1039/c6em00408c, 2016.

Moor, K. J., Schmitt, M., Erickson, P. R., and McNeill, K.: Sorbic Acid as a Triplet Probe: Triplet Energy and Reactivity with Triplet-State Dissolved Organic Matter via 1O2 Phosphorescence, Environ. Sci. Technol., http://dx.doi.org/10.1021/acs.est.9b01787, 2019.

Mu, Z., Chen, Q. C., Wang, Y. Q., Shen, Z. X., Hua, X. Y., Zhang, Z. M., Sun, H. Y., Wang, M. M., and Zhang, L. X.: Characteristics of Carbonaceous Aerosol Pollution in PM2.5 in Xi'an, Huan Jing Ke Xue, 40, 1529-1536, http://dx.doi.org/10.13227/j.hjkx.201807135, 2019.

Murphy, K. R., Stedmon, C. A., Waite, T. D., and Ruiz, G. M.: Distinguishing between terrestrial and autochthonous organic matter sources in marine environments using fluorescence spectroscopy, Mar. Chem., 108, 40-58, http://dx.doi.org/10.1016/j.marchem.2007.10.003, 2008.

Murphy, K. R., Stedmon, C. A., Graeber, D., and Bro, R.: Fluorescence spectroscopy and multi-way techniques. PARAFAC, Anal. Methods, 5, 6557-6566, http://dx.doi.org/10.1039/c3ay41160e, 2013.

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. Tech., 52, 11243-11250, http://dx.doi.org/10.1021/acs.est.8b02648, 2018.

Paul Hansard, S., Vermilyea, A. W., and Voelker, B. M.: Measurements of superoxide radical concentration and decay kinetics in the Gulf of Alaska, Deep Sea Res., Part I, 57, 1111-1119, http://dx.doi.org/10.1016/j.dsr.2010.05.007, 2010.

Perri, M. J., Seitzinger, S., and Turpin, B. J.: Secondary organic aerosol production from aqueous photooxidation of glycolaldehyde: Laboratory experiments, Atmos. Environ., 43, 1487-1497, http://dx.doi.org/10.1016/j.atmosenv.2008.11.037, 2009.

Powers, L. C., Babcock-Adams, L. C., Enright, J. K., and Miller, W. L.: Probing the photochemical reactivity of deep ocean refractory carbon (DORC): Lessons from hydrogen peroxide and superoxide kinetics, Mar. Chem., 177, 306-317, 10.1016/j.marchem.2015.06.005, 2015.

Richards-Henderson, N. K., Pham, A. T., Kirk, B. B., and Anastasio, C.: Secondary organic aerosol from aqueous reactions of green leaf volatiles with organic triplet excited states and singlet molecular oxygen, Environ. Sci. Technol., 49, 268-276, http://dx.doi.org/10.1021/es503656m, 2015.

Rosado-Lausell, S.L., Wang, H.T., Gutierrez, L., Romero-Maraccini, O.C., Niu, X.Z., Gin, K.Y.H., Croue, J.P., Nguyen, T.H.: Roles of singlet oxygen and triplet excited state of dissolved organic matter formed by different organic ~~matters~~ in bacteriophage MS2 inactivation, Water Res., 47, 4869-4879, http://dx.doi.org/10.1016/j.watres.2013.05.018, 2013.

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.

Saleh, R., Hennigan, C. J., McMeeking, G. R., Chuang, W. K., Robinson, E. S., Coe, H., Donahue, N. M., and Robinson, A. L.: Absorptivity of brown carbon in fresh and photo-chemically aged biomass-burning emissions, Atmos. Chem. Phys., 13, 7683-7693, http://dx.doi.org/10.5194/acp-13-7683-2013, 2013.

Sharpless, C. M.: Lifetimes of Triplet Dissolved Natural Organic Matter (DOM) and the Effect of NaBH4 Reduction on Singlet Oxygen Quantum Yields: Implications for DOM Photophysics, Environ. Sci. Technol., 46, 4466-4473, http://dx.doi.org/10.1021/es300217h, 2012.

Sierra, M. M. D., Giovanela, M., Parlanti, E., and Soriano-Sierra, E. J.: Fluorescence fingerprint of fulvic and humic acids from varied originsas viewed by single-scan and excitation/emission matrix techniques, Chemosphere, 58, http://dx.doi.org/10.1016/j.chemosphere.2004.09.038, 2005.

Smith, J. D., Sio, V., Yu, L., Zhang, Q., and Anastasio, C.: Secondary organic aerosol production from aqueous reactions of atmospheric phenols with an organic triplet excited state, Environ. Sci. Technol., 48, 1049-1057, http://dx.doi.org/10.1021/es4045715, 2014.

Szymczak, R., and Waite, T.: Generation and decay of hydrogen peroxide in estuarine waters, Mar. Freshwater Res., 39, 289-299, http://dx.doi.org/10.1071/MF9880289, 1988.

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.

Tang, S. S., Li, F. H., Tsona, N. T., Lu, C. Y., Wang, X. F., and Du, L.: Aqueous-Phase Photooxidation of Vanillic Acid: A Potential Source of Humic-Like Substances (HULIS), Acs Earth and Space Chem., 4, 862-872, http://dx.doi.org/10.1021/acsearthspacechem.0c00070, 2020.

Vodacek, A., Blough, N. V., DeGrandpre, M. D., Peltzer, E. T., and Nelson, R. K.: Seasonal Variation of CDOM and DOC in theMiddle Atlantic Bight: Terrestrial Inputs and Photooxidation, Limnol. Oceanogr., 42, 231-253, http://dx.doi.org/10.1117/12.26643, 1997.

Wenk, J., von Gunten, U., and Canonica, S.: Effect of dissolved organic matter on the transformation of contaminants induced by excited triplet states and the hydroxyl radical, Environ. Sci. Technol., 45, 1334-1340, http://dx.doi.org/10.1021/es102212t, 2011.

Wenk, J., Aeschbacher, M., Salhi, E., Canonica, S., von Gunten, U., and Sander, M.: Chemical oxidation of dissolved organic matter by chlorine dioxide, chlorine, and ozone: effects on its optical and antioxidant properties, Environ. Sci. Technol., 47, 11147-11156, http://dx.doi.org/10.1021/es402516b, 2013.

Wong, J. P. S., Zhou, S. M., and Abbatt, J. P. D.: Changes in Secondary Organic Aerosol Composition and Mass due to Photolysis: Relative Humidity Dependence, J. Phys. Chem. A, 119, 4309-4316, http://dx.doi.org/10.1021/jp506898c, 2015.

Zappoli, S., Andracchio, A., Fuzzi, S., Facchini, M. C., Gelencser, A., Kiss, G., Krivacsy, Z., Molnar, A., Meszaros, E., Hansson, H. C., Rosman, K., and Zebuhr, Y.: Inorganic, organic and macromolecular components of fine aerosol in different areas of Europe in relation to their water solubility, Atmos. Environ., 33, 2733-2743, http://dx.doi.org/10.1016/S1352-2310(98)00362-8, 1999.

Zepp, R. G., Schlotzhauer, P. F., and Sink, R. M.: Photosensitized transformations involving electronic energy transfer in natural waters: role of humic substances, Environ. Sci. Technol., 19, 74-81, http://dx.doi.org/10.1021/es00131a008, 1985.

Zhang, D., Yan, S., and Song, W.: Photochemically induced formation of reactive oxygen species (ROS) from effluent organic matter, Environ. Sci. Technol., 48, 12645-12653, http://dx.doi.org/10.1021/es5028663, 2014.

Zhao, R., Lee, A. K. Y., Huang, L., Li, X., Yang, F., and Abbatt, J. P. D.: Photochemical processing of aqueous atmospheric brown carbon, Atmos. Chem. Phys., 15, 6087-6100, http://dx.doi.org/10.5194/acp-15-6087-2015, 2015.

Zhong, M., and Jang, M.: Dynamic light absorption of biomass-burning organic carbon photochemically aged under natural sunlight, Atmos. Chem. Phys., 14, 1517-1525, http://dx.doi.org/10.5194/acp-14-1517-2014, 2014.

Zhou, H., Yan, S., Lian, L., and Song, W.: Triplet-State Photochemistry of Dissolved Organic Matter: Triplet-State Energy Distribution and Surface Electric Charge Conditions, Environ. Sci. Technol., 53, 2482-2490, http://dx.doi.org/10.1021/acs.est.8b06574, 2019.