Photodegradation of Atmospheric Chromophores: Changes in Oxidation State and Photochemical Reactivity

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Abstract: Atmospheric chromophoric organic matter (COM) can participate in photochemical reactions because of the photosensitivei~~ness~~ty, thus COM ha~~ve~~s a potential contribution to aerosols aging. However, ~~T~~thehe~~ photochemical mechanism of atmospheric COM and the~~ effect of COM photo-degradation on~~ its ~~ photochemical reactivity and aerosol aging are not fully understood. Here, we report the~~ characteristics of COM photo-degradation, the ~~ potential ~~effects ~~impacts of ~~COM ~~ photo~~lysis~~degradation on carbonaceous components, optical properties, fluorophores components, and ~~ the ~~photochemical reactivity~~, and the contribution of COM to reactive oxygen species (ROS)~~. ~~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~~degraded, and fluorescent intensities~~ a~~ decrease by~~n average ~~ 70% on average~~ of fluorescence intensities are lost after 7 days of light exposure~~. Furthermore, ~~there is a transformation from ~~low oxidation humic-like substance (HULIS) is converted into~~to~~ high oxidation HULIS~~HULIS and~~, the result suggests that~~ ~~ oxidation of ~~high oxidation ~~HULIS ~~could ~~can be used to trace the degree of aerosols aging. COM Photodegradation has a significant impact on ~~ In terms of~~ photochemical reactivity. The content of ~~, compared with before photolysis, the t~~triplet state COM ~~(^{3}COM*) ~~ decreases slightly in ambient particulate matter ~~ (ambient PM) samples, but ~~but increases in primary organic aerosol~~ (POA)~~ following photodegradation. The result~~ also ~~ highlight that photodegradation has opposite effect on different~~ the photochemical mechanisms and aerosol aging processes are relatively different in various~~ aerosols as a result of the changes in components. The ability of COM generating singlet oxygen declines~~. Photolysis and conversion of COM reduce photochemical activity~~ obviously~~,~~, which is consistent with optical properties. Photodegradation of precursors limit singlet oxygen generation and affect the aerosol photochemistry process. ~~so that COM induce less singlet oxygen. ~~In conclusion, COM photo-degradation~~ of COM~~ not only change the~~ chemical ~~ compositions and properties, but also change~~ the roles of the COM in ~~ aerosol aging.

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

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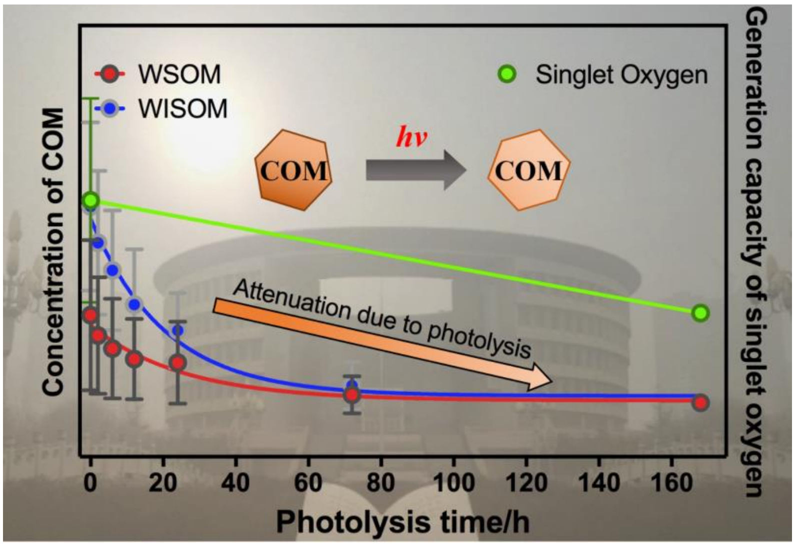


1. Introduction

Atmospheric ~~Chromophoric~~ chromophoric organic matter (~~– (COM) widely exists in the atmospheric environment.~~ COM) ~~are~~ mainly originate from~~derived from~~ biomass combustion emissions and secondary ~~chemistry~~ aerosols~~reactions~~ (Andreae ~~and~~ & Gelencser, 2006; Budisulistiorini et al., 2017; Graber ~~and~~ & Rudich, 2005; Zappoli et al., 1999). Because of the significant absorption for ~~short~~ short-wave~~ radiation~~ radiation ~~–~~(~~the~~ Wavelength range ~~of~~ from near-ultraviolet light to visible light) (Rosario-Ortiz and Canonica, 2016; Cheng et al., 2016), COM may undergo ~~photolyze~~photochemical process and have a significant impact on atmospheric components and quality~~, convert components and induce reactive substances~~ (Zhao et al., 2013; Jo et al., 2016~~Chen et al., 2018; Wenk et al., 2011; Maizel et al., 2017~~). Therefore,~~–~~ simulation and evaluation of COM photochemistry is necessary for understanding aerosol aging.

As photosensitive substances~~ in aerosol~~, ~~the~~ the optical properties ~~physical~~ and ~~chemical characteristics~~ components of COM change significantly under ~~s~~s~~unlight exposure~~olar irradiation (Alkinson et al., 2016; Carlton et al., 2007; ~~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~~). On the one hand, ~~The specific impacts are summarized. (1) Changes in optical characteristics. Sunlight exposure cause the photo-bleaching of COM. Previous studies reported that~~ optical properties ~~chromophores produced by wood-burning were significantly~~change significantly due to chromophores are photo-bleached in aerosols. For example, ~~(~~Lee et al. (~~,~~2014) reported that the mass absorption coefficents (MAE) of second organic aerosol (SOA) continue to decrease in the UV-Vis spectral; Zhong and Jang~~,–~~ (2014) illustrated that MAC decreased by 41% on average because of the bleaching of wood-burning OM. The reason was the major components of wood-burning OM, such as conjugated aromatic rings and phenols, and hydroxyl groups, could be photodegraded.~~. 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.~~ On the other hand, ~~(2) Changes in chemical composition. P~~photodegradation~~hotochemistry~~ has a significant effect on the composition of COM. Photodegradation ~~Photolysis~~ can cause that COM decompose into small molecules and COM may have lower volatility and higher oxidation degree after photodegradation~~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.~~ , which could be attributed to the formation of SOA during the photochemical reaction process. For example, Oligomeric COM could be generated by a mixture of anthracene and naphthalene suspensions through self-oxidation under solar irradiation and 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). Previous studies (Zhong & Jang, 2014; Saleh et al., 2013; Harrison et al., 2020) also have illustrated that SOA may have a more significant ability on light absorption than POA in the short-wavelength visible and near-UV region. ~~For example, oligomeric COM could be generated by a mixture of anthracene and naphthalene suspensions 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).~~ As a result, photochemical process may play an important role in the components and properties of COM. Changes in chemical composition and optical properties also have a significant impact on ~~affect~~ photochemical activity in turn. There are limited studies that comprehensive exploring the components and properties transformation of COM in aerosols during the photodegradation processes. ~~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 could ~~not only decompose and transform, but also~~ participate in the complex photochemical reaction, which further affect the aerosol aging (~~Malley~~ Mang et al., ~~2017~~2008). On the one hand, COM ~~could~~ participates in atmospheric photochemical processes as a reactant~~directly~~. For example, ~~–~~ COM can be oxidized by hydroxyl radicals (•OH) (Zhao et al., 2015) and the formation of polyols can be attributed to photooxidation of isoprene, which could be initiated by •OH (Claeys et al., 2004)~~excited COM react with organic matter and generate secondary organic aerosols (Zhao et al., 2015; Saleh et al., 2013; Zhong and Jang, 2014; Lee et al., 2014; Liu et al., 2016)~~. Humic-like substance (HULIS) with complex functional groups has significant contribution to photochemistry (George et al., 2015; Nebbioso & Piccolo, 2013; Wenk et al., 2013). ~~Various secondary photochemistry 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~~ participates in atmospheric

~~photochemical~~ photochemistry ~~reactions~~ process indirectly through ~~inducing~~ generating reactive intermediates~~species~~. Upon light absorption, high-energy singlet state COM (^{1}COM*) could be generated. ^{1}COM* deactivate quickly with the ways of emitting photon (fluorescence) and intersystem crossing (triplet state, ^{3}COM*). ^{3}COM* can generate reactive oxygen species (ROS), such as singlet oxygen ($^1O_2$), super oxide (•O_2^-) and •OH, which indicate that ^{3}COM* play a critical role in ROS formation and pollutant attenuation (Paul Hansard et al., 2010; Szymczak & Waite, 1988; Zhang et al., 2014; Rosario-Ortiz and Canonica, 2016; Sharpless, 2012; Haag and Gassman, 1984; Zhou et al., 2019). A lot of DOM, such as ~~Aromatic~~ aromatic ketones (Canonica et al., 2006; Marciniak et al., 1993), benzophenone (Encinas et al., 1985), and phenanthrene (Wawzonek & Laitinen, 1942), ~~could be~~have been identified as the precursor of ~~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)~~. Probes, such as 2,4,6-trimethylphenol (TMP) and sorbic acid (SA), are applicable to evaluate ~~3COM* induce reactive oxygen species (ROS), such as singlet oxygen (1O2), super-oxygen (•O2-) 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 DOC through simultaneous measuring the rates of both H2O2 and O2− photoproduction in laboratory.~~ the chemical reactivity (Zhou et al., 2019; Moor et al., 2019; Chen et al., 2021). Why ^{3}COM* is employed not ^{1}COM*? The reasons are lower formation rate (15–100 times slower than ^{1}COM*), lower quenching rate (20000 times lower than ^{1}COM*), and highter steady-state concentrations of ^{3}COM* (200~1300 times higher than ^{1}COM*) (McNeil et al., 2016). Considering the potential effect of COM on aerosol aging and quality, ~~It~~ it is necessary to clarify the path and mechanism~~effect of COM driving aerosol aging~~.~~, but the path and effect are both unclear.~~

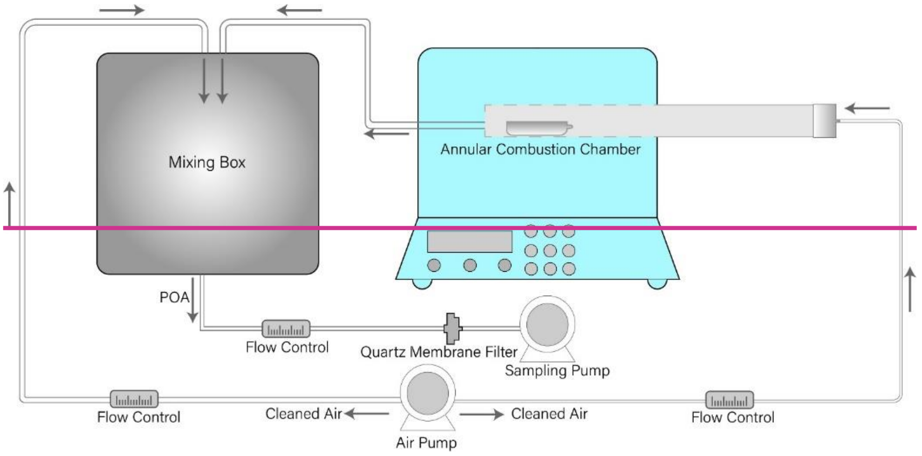
COM photochemistry may dominate ~~T~~the chemical composition and ~~atmospheric quality~~aerosol aging ~~are significantly affected by aerosol aging~~. In order to illustrate the properties of COM photodegradation and the effect of COM ~~photolysis~~ photodegradation on aerosol aging, we simulate the process of COM ~~photolysis~~ photodegradation and COM ~~inducing~~ generating ROS ~~in primary organic aerosol (POA) and ambient particulate matter (ambient PM)~~ in laboratory. The objectives of the study are (1) to clarify ~~The~~ the characteristics of carbonaceous components variation during COM photodegradation process, (2) to explore the effects of photo-degradation ~~in~~ on the fluorophores and optical properties of water-soluble and water-insoluble chromophores ~~are clarified by the approach of excitation-emission matrices (EEM) combined with parallel factor analysis (PARAFAC).~~, and (3) to investigate ~~The~~ the effects of COM photodegradation 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 altitude of sampling ~~device~~ location is about 30 m~~ from the ground~~). The ambient PM samples were collected on 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-burning samples were ~~chosen to generate aerosols~~collected~~.~~ (Schematic diagrams of combustion equipment is~~ As~~ shown in **Fig~~.~~ure S1**~~, ~~). ~~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 particle matter entered the mixing box. The clean air was 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 (Pall life sciences, Pall Corporation, America) with a diameter of 37 mm.~~ The POA samples were stored in the refrigerator at -20 °C prior to use.

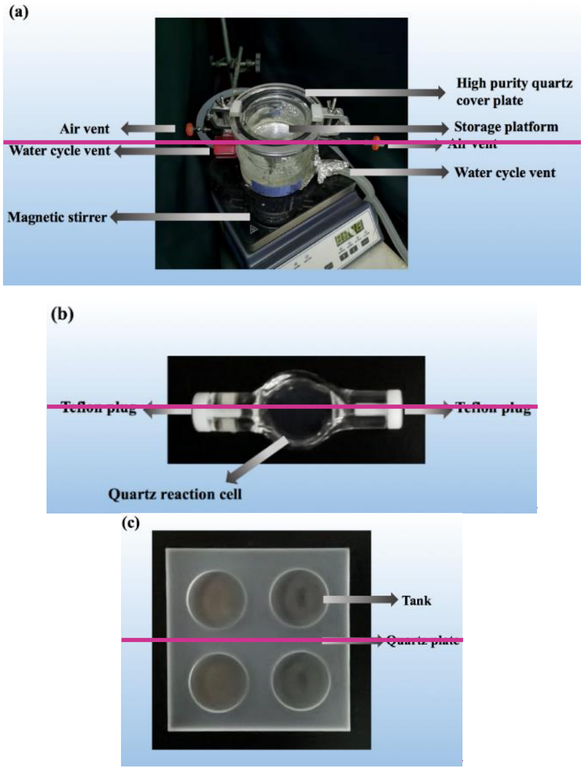


~~**Fig.1** Schematic diagrams of combustion equipment for POA.~~

2.2 ~~Photolysis~~ Photodegradation experiment

~~The material of reactor is quartz (**Fig.2a**) and t~~A~~he~~ quartz reactor was designed for photolysis experiment (Schematic diagrams of the photochemical devices are shown in **Figure S2**~~.~~; The detail of the reactor has been described in previous study (Chen et al., 2021)). ~~The reactor was sealed through clamping a quartz cover to reactor. Two air vents was 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. 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 illumination times were 0 h, 2 h, 6 h, 12 h, 24 h, 3 d and 7 d, respectively. ~~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~~ Two capsules (**Figure S2(b) & (c)**) ~~small storage platform~~were designed for triplet state and ROS generation experiment~~was placed in the reactor 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.2** Schematic diagrams of the photochemical devices. (a) The reactor is used for maintaining the reaction environment. (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 mm².~~ ~~The size of the tanks is a radius of 5.6 mm and a depth of 2.5 mm.~~

2.3 *Carbonaceous components analysis*~~*Sample extraction*~~

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

~~*2.4 OC/EC analysis*~~

The analytical method of carbonaceous components~~organic carbon (OC)~~ ~~analysis could refer to the~~has been described previous~~ literature~~ly (Mu et al., 2019). Briefly, 100 μL~~ of~~ extracts were injected on the ~~clean~~ baked quartz filter. Then, the wet filters were dried out by a rotary evaporator and the dried filters~~. 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 uncertainty of the method was <3.7% (one standard deviation).

2.~~5~~ 4 Optical analysis

The light absorption and EEM spectra of the extracts were 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 emission wavelength was 250-800 nm. The interval was 5 nm. The exposure time was 0.5 s. The absorption spectra were also recorded in the wavelength range of 200-600 nm. Water and methanol background samples were measured using the same method and the background signals were subtracted from the sample signals. The extracts were diluted to reduce internal filtration effect (The concentrations and dilution factors are shown in **Table S2** of SI).

The EEM data was analyzed by the PARAFAC model to identify fluorophores (The detailed analysis process refers to the previous papers~~)~~, (Murphy et al., 2013; Chen et al., 2016a; Chen et al., 2016b~~; Chen et al., 2016a~~))). ~~111 samples were used to create the model.~~ WSOM and WISOM (111 samples) were combined in the dataset to create the PARAFC model. ~~Briefly, a~~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~~ S4** of SI).

2.~~6~~ 5 Triplet state generation experiment

As short-lived reactive intermediates, ^{3}COM* have an important impact on photochemical process in atmospheric environment (Kaur et al., 2018). Therefore, changes in ~~The triplet states~~^{3}COM* generation ability before and after ~~photolysis~~ photodegradation were studied. Chemical probe 2,4,6-trimethylphenol (TMP) was used as the capturing agent for the triplet state. 60 μL of WSOM extracts (WSOC concentrations are shown in **Table S3**) and 60 μL of TMP solution (c_{TMP} = 20 μM, Aladdin, China) were mixed in the capsule~~cell~~ (**Fig~~.~~ure ~~2b~~S2(b)**). The capsule~~ cell~~ ~~was~~ was placed in the reactor (**Fig~~.~~ure ~~2a~~S2(a)**)~~ 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. Then 90 μL mixed solution was taken out from the capsule~~ cell~~ at different time points~~. Then~~ and 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).~~

TMP was quantified by liquid chromatography (LC). The~~ analyzed ~~ ~~parameters~~ method 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 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}):

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

2.~~7~~ 6 ~~Triplet state driving s~~Singlet oxygen generation experiment

The effects of the COM ~~photolysis~~ photodegradation on singlet oxygen were studied. 4-Hydroxy-2, 2, 6, 6-tetramethylpiperidine (TEMP, c_{TEMP}=240 mM, Aladdin, China) was used as the capturing agent ~~of~~ for 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 capsule~~ tanks~~ (**Figure S2(~~.2c~~c)**).~~ The mixed solution was placed in the reactor (**Fig.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~~capsule 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~~capsule was illuminated ~~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 capsule~~ mixed solution~~ was~~ placed~~ illuminated ~~–~~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~~COM can be decomposed and transformed in aerosol due to photodegradation ~~illumination~~ (Wong et al., 2015). **Fig.~~3~~ 1** describes the ~~variable characteristics~~changes in the content of~~ total organic carbon and~~ carbonaceous components before and after COM ~~photolysis~~photodegradation. In POA, ~~The results show that both water-soluble and water-insoluble organic matter undergo partial photolysis in POA samples~~ w~~(**Fig.3A**), with~~ater soluble and water insoluble organic carbon (WSOC and WISOC)~~ an average ~~ decrease ~~of~~ by 22.1% and 3.5%, respectively. The results suggest that WSOC tend to be photodegraded in POA. As shown in **Fig.1(A)**, the proportion of OC1 in WSOC (OC1 and OC2-4 are the different stage in the process of thermal-optical analysis) decreases significantly, which is the main loss of OC. OC1 are characterized by small molecular weight and highly volatile (Karanasiou et al., 2015). The result suggests that OC with small molecular weight and highly volatile tend to be photodegraded. In WISOC, there is a process of OC1 translating into pyrolysis carbon (OPC). OPC in WISOM show an increasing trend (an average increase of 2.4 times). The pyrolysis carbon is oxygen-containing substance. Thus, the increasing oxygen-containing organic matter may be due to the photo-inducing oxidation reaction.

POA is fresh and ambient PM have undergone aerosol aging. In ambient PM (**Fig.1B**), WSOC is nearly unchanged and WISOC decreases by 18.2%, which is opposite to 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.3B**).~~The results reflect that WSOC has been photodegraded completely following the photodegradation and mineralization process in ambient PM. However, WISOC with high molecular weight could not be photodegraded completely and continue to be photodegraded in laboratory.

~~Photolysis also results in the variation on carbonaceous components. In POA (**Fig.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 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. ~~T~~In contrast to POA, t~~he proportions of ~~carbonaceous components~~OC1, OC2-4, and OPC are relatively stable in ambient PM~~ (**Fig.3B**)~~, which indicate that the decreasing proportion in the different stage are similar and the tendency is also opposite to POA. The result ~~The result ~~reflects that~~ ambient PM samples ~~ different carbonaceous components have the similar abilities of photodegradation in ambient PM. Organic matter with high molecular weight is photocomposed to small molecular weight and the molecular weight tend to be consistent following the photodegradation~~have been subjected to sufficient atmospheric oxidation, so organic matter are not decomposed or oxidized again~~.

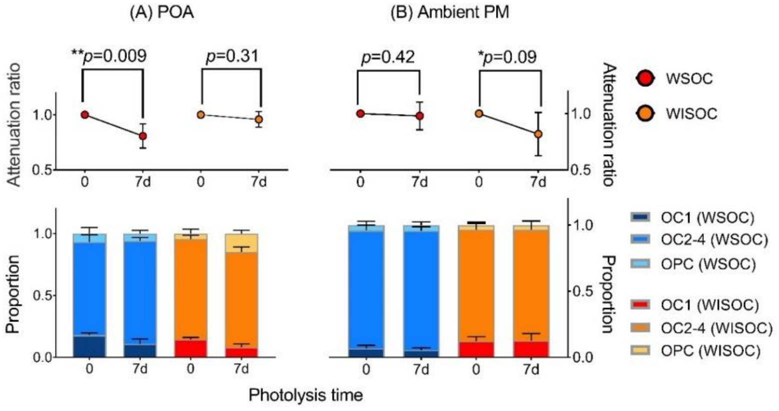


Fig.~~3~~ 1 ~~Variations of~~Changes in~~ total carbon and~~ carbonaceous components before and after ~~photolysis~~photodegradation. The *p*-value is the probability that two sets of data have the same level (two-tailed test). * and ** are represent the significant difference at the 0.1 and 0.01 levels, respectively.

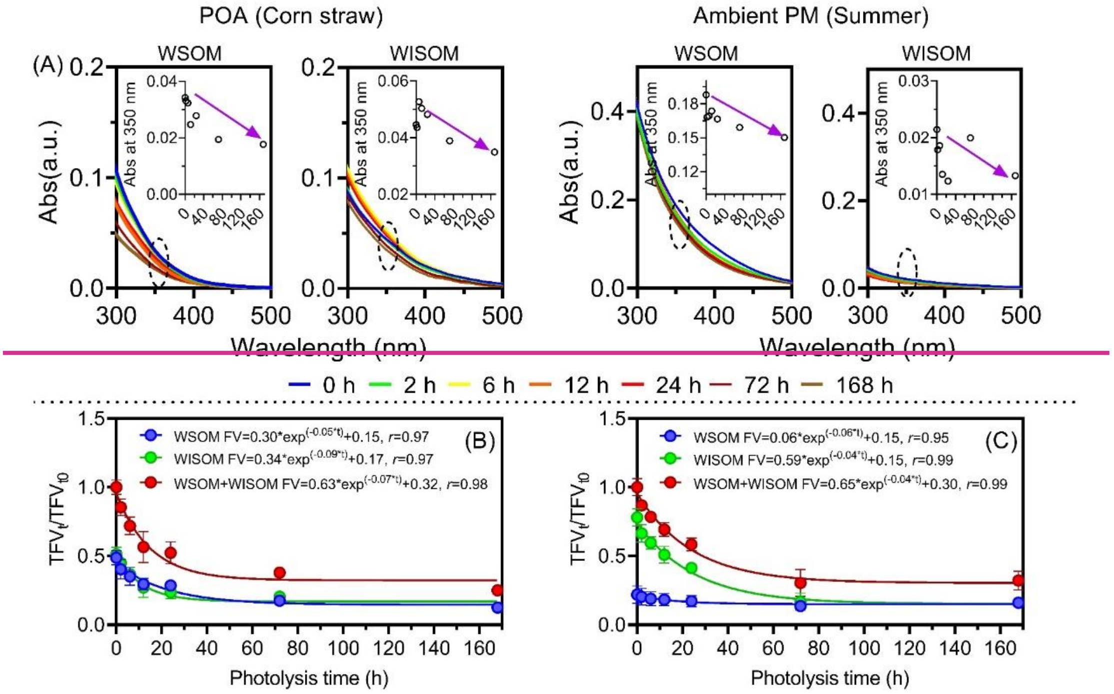
3.2 Effect of COM photo~~-~~degradation on optical properties

As shown in **Fig.2**, ~~Both~~ both ~~absorbance~~ absorption coefficients and total fluorescence volume (TFV, RU-nm^2/m^3) significantly decrease ~~dur~~following~~ing~~ aerosol photo~~lysis~~degradation ~~(Fig.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 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~~which suggest that COM are photo-bleached (Aiona et al., 2018; Duarte et al., 2005; Liu et al., 2016). ~~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**, t~~The ~~attenuation~~attenuations of fluorescence and absorption coefficients are fit to first-order decay. ~~is mathematical analyzed~~ The absorption coefficients decrease by 32.0% and TFV decreases by 71.4% on average~~and the number or shape of fluorophores do not change during COM photolysis~~. However, as shown in **Fig.3**, fluorescence intensities increase and decrease in different regions of EEMs (Aiona et al., 2018; Timko et al., 2015).

In POA (**Fig.~~4B~~2(B)**), TFV decreases by 74.8% on average and the attenuation ~~characteristics of water-soluble and water-insoluble components~~ are fitted with first-order decay kinetics~~similar~~. The attenuations of TFV are significant similarities between WSOM and WISOM. Significantly, compared with most POA samples, the fluorescence intensity of wood-burning COM only decreases by 9.0% (**Figure S7**), which is due to TFV of WISOM remain almost unchanged. Secondary water-insoluble organic substances may be generated slightly in wood-burning COM (Zhong & Jang, 2014).~~However, 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 also depend on the types and water-insoluble wood-burning COM are difficultly photodegraded. In addition, ~~of~~ fluorophores~~COM~~ photodegradation depend on ~~and~~ the photochemical environment, such as solution pH (Aiona et al., 2018), salinity (Xu et al., 2020), and temperature (Yang et al., 2021).

In ambient PM (**Fig.2(C)**), ~~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 of TFV and WISOC (section 3.1) are similar in wood burning samples, which~~

~~probably attribute to the slight generation of secondary water-insoluble organic substances. T~~the ~~characteristics~~ decay rate constant of TFV ~~attenuation~~ in ambient PM (~~rate constant~~ k = 0.04 h^{-1}) is ~~different from~~lower than in POA (k = 0.07 h^{-1}). ~~Compared with water-soluble chromophores, the water-insoluble chromophores photo-decompose obviously and the~~ TFV of water-soluble fluorophores decreases by ~~79.1~~79.4~~%,~~ % but water-soluble fluorophores~~chromophores~~ decreases by~~only~~ ~~21~~26.7%~~.9% on average~~. ~~The results suggest that COM have undergone a long-term atmospheric aging and water-soluble COM have greater ability to be photolyzed~~The attenuation of TFV and carbonaceous components are identical with each other. The results suggest that water-insoluble fluorophores have greater ability to be photodegraded than water-soluble fluorophores in ambient PM. It is worth noting that 72 h could be consider as the end point of aerosol aging because TFV maintain a constant value after 72 h in POA and ambient PM.~~.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.~~



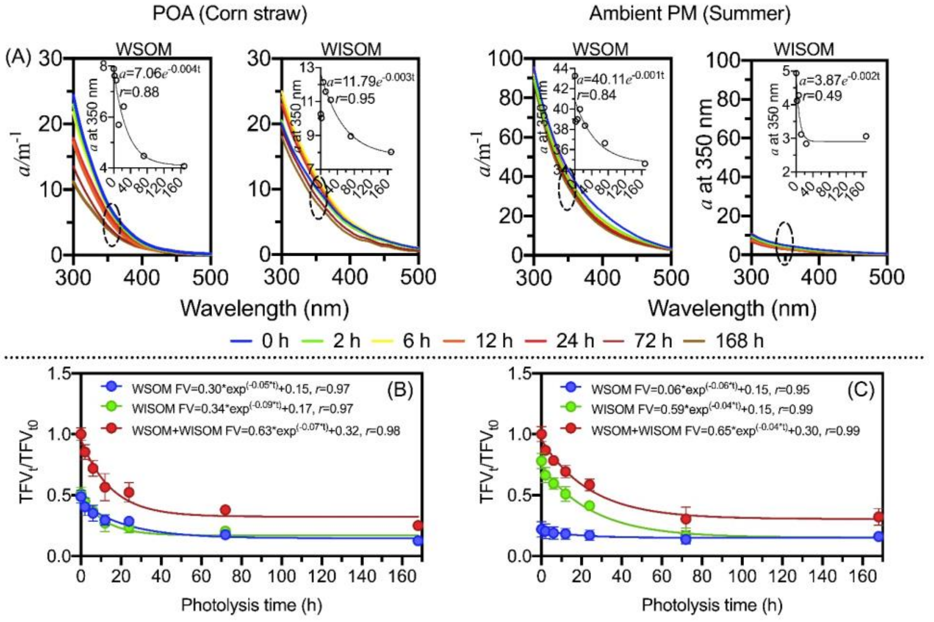


Fig.~~4~~ **2** ~~The c~~Changes ~~of~~ in light absorption and fluorescence volume during the ~~photolysis~~ photodegradation process. (A) ~~The light a~~Absorption ~~spectrum~~coefficient. The scatter plot is absorption coefficient~~changes in Abs~~ at 350 nm. (B) and (C) ~~show~~ the attenuation curve of ~~average~~ fluorescence volume ~~of~~ in 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~~Fluorophores compositions ~~variations~~ are studied by the approach of EEMs-PARAFAC (**Fig.~~5A~~3A**). ~~Tang et al. (2020)~~ Although previous ~~study~~ study analyzed the water-soluble and water-insoluble ~~chromo~~fluoro~~phores~~phores ~~in water-soluble and water-insoluble samples, respectively~~ separately (Tang et al., 2020a)~~. However, b~~, based on the Chen's ~~study~~ studies (~~2020~~2020; 2016b), water-soluble and water-insoluble samples were combined to create the PARAFAC model ~~so that~~to illustrate the distribution of fluorophores~~chromophores~~ in WSOM and WISOM and solvent had no significant effect on the EEMs of complex mixtures in aerosols. Four fluorophores are identified. Four fluorophores are identified. The fluorescence peaks of C1 and C2 appear at (Ex./Em. = 224/434 nm) and (Ex./Em. = 245/402 nm~~),~~). ~~and t~~The peaks are similar to high and low oxidation humic-like substance (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 fluorophores ~~were~~ are associated with protein-like organic matter (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 content of ~~The compositions of~~ fluorophores~~chromophores~~ changes significantly during the photodegradation~~lysis~~ process. In POA (**Fig.~~5B~~3B**), the content of high-oxidation HULIS (C1) increases significantly in ~~water-soluble component~~WSOM and the relative content increases by 25.7% on average. ~~On the contrary, l~~Low oxidation HULIS (C2) and PLOM (C3&C4) decrease by 6.0% and 19.7%, respectively. ~~The~~Changes in ~~–~~proportion ~~variation~~ indicates that high-oxidation HULIS fluorophores (C1)~~chromophores~~ could be generated and low oxidation HULIS(C2) and PLOM ~~chromophores~~ (C3&C4) may be photolyzed, which suggest that low oxidation HULIS (C2) could be converted into high oxidation HULIS (C1) due to photooxidation ~~–~~(Tang et al., 2020b; Chen et al., ~~2020~~2020). Furthermore, ~~Not only in water-soluble chromophores, t~~the content of high-oxidation HULIS (C1) also increases ~~in water-insoluble chromophores~~ (average 17.5%)~~ and low-oxidation HULIS also decrease~~ in WISOM, which can be attributed to photo-mediated secondary reaction~~in water-insoluble chromophores~~.

~~–~~In ambient PM (**Fig.3C**), the content of PLOM (C3&C4) in ambient PM (43.3%) is significantly lower than that in POA (19.4%). The ~~the~~ content of high-oxidation HULIS increases and the low-oxidation HULIS decreases~~ (**Fig.5C**)~~, which are similar to POA. ~~which reveal that low-oxidation HULIS could be transformed into high-oxidation HULIS (Chen et al., 2016a). T~~Thus, high-oxidation HULIS could be used to trace the degree of aerosols aging.

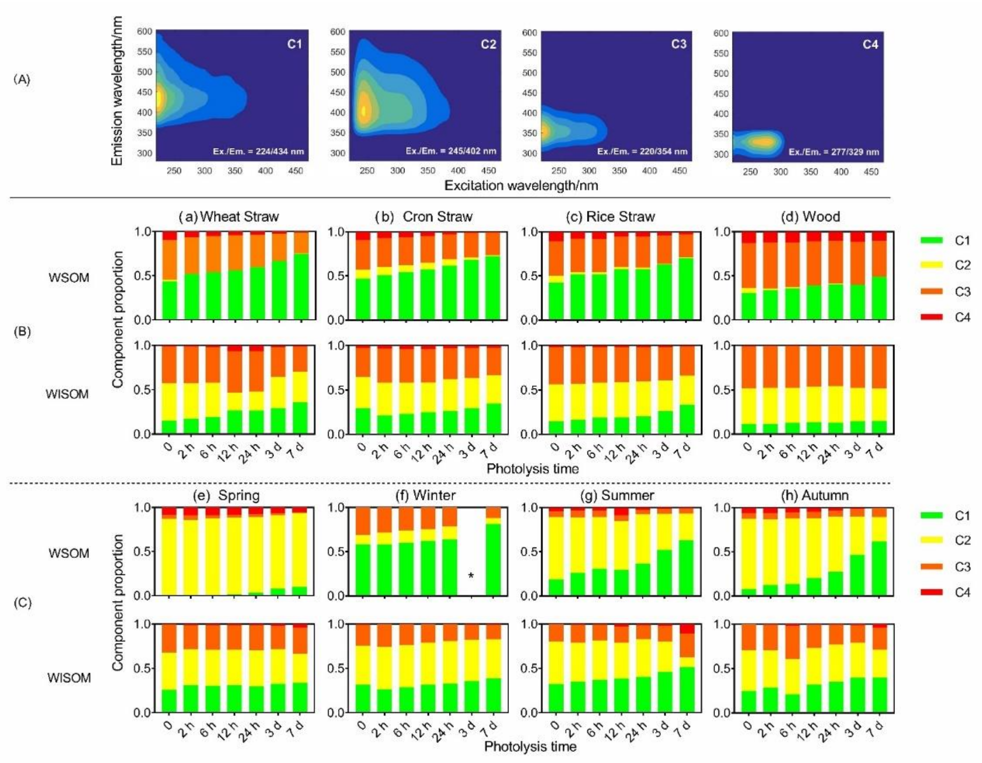


Fig.~~5~~ 3 (A) ~~The~~ EEM spectra of ~~chromophores~~fluorophores; (B) ~~is~~ ~~the variation characteristics of~~ Changes in proportion of fluorophores ~~chromophores~~ in POA; (C) Changes in proportion of fluorophores ~~is the variation characteristics of chromophores~~ in ambient PM. *: The data 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~~yield of ^{3}COM* and ~~singlet oxygen~~$^1O_2$. **Fig.**~~6~~ 4 show the difference of triplet state generation ~~capability~~ before and after the ~~photolysis~~ photodegradation (Details are shown in **Figure S**8~~6 of SI~~). In ambient PM, the generation rate of triplet state ~~is~~ ~~decreased~~ decreases by 11% on average after COM photodegradation~~photolysis~~, while statistical analysis shows that the changes of triplet state generation~~photo-degradation~~ ~~does~~ are not ~~significantly~~obvious ~~affect the~~ ~~triplet state generation~~ (p = 0.38, two-tailed test). On the contrary, photodegradation promote triplet state generation significantly, the triplet state~~s~~ generation rate ~~markedly~~ increases by 75% on average in POA (p = 0.07, two-tailed test)~~, which indicate that photo-degradation significantly promote triplet state generation~~. ~~COM are photo-decomposed, while~~ T~~the t~~riplet state generation ~~ability~~ remains unchanged or increases following photodegradation. The results are ~~not as~~ unexpected~~.~~ ~~However, t~~and ~~he result~~ can be explained by recent study (Chen et al. ~~2020~~ 2021~~for ACPD~~): On the one hand, only a small ~~number~~ proportion of ~~chromophores~~ COM ~~have the ability to~~ could generate triplet state~~s~~ in aerosols and~~.~~ ~~The~~Fluorophores ~~decomposition of most chromophores~~ does not represent the ~~decomposition of these~~ ~~specific types of chromophores~~COM with the ability to generate triplet state. Therefore, triplet state generation could not be evaluated by fluorescence intensity. On the other hand, ~~We~~ we use a high concentration of TMP, in this case, TMP mainly capture ~~-short-lived~~high-energy triplet state (Rosado-Lausell et al., 2013; Chen et al., 2021). Thus, ~~chromophores~~ COM, that ~~can~~ could ~~form~~ generate a high-energy~~short-lived~~ triplet state, may not be ~~reduced~~ photodegraded~~or even generated during the photolysis process~~.

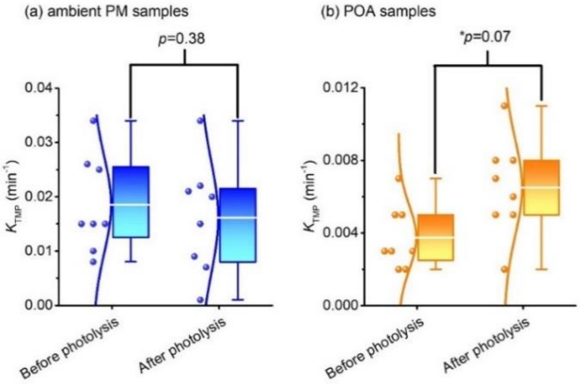


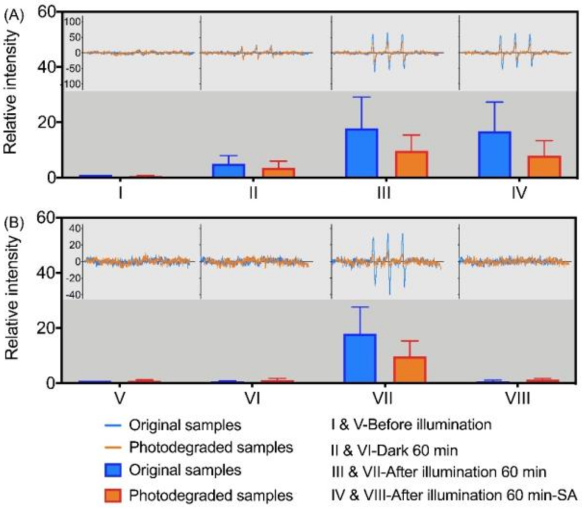
Fig.~~6~~ 4 ~~The c~~Changes in~~of~~ the triplet state generation~~-capacity in~~. (a) ~~ambient~~ Ambient PM~~-and~~; (b) POA~~-samples before and after photolysis~~. The line from bottom to top in the box plots are minimum, first quartile, the average value (white lines), third quartile, and maximum, 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 state~~s~~ and further~~ly~~ ~~induce~~ generate singlet oxygen ~~-~~(McNeill and Canonica, 2016). The effect~~s~~ of COM photo~~-~~degradation on singlet oxygen ~~are~~ is ~~illustrated~~ studied~~using chemical capture and EPR analysis~~. Typical EPR spectra of $^1O_2$ are shown in **Fig.~~7~~ 5** (EPR spectra of all samples are shown in **Figure ~~S7~~ S9** and **Figure ~~S8~~S10**). ~~More narrowly, i~~In the original POA samples (i.e., the original samples~~the sample~~ with ~~photolysis~~ photodegradation time ~~is~~ of 0, the photodegraded samples with photodegradation time of 7d; details of samples are described in section 2.2),

In POA, (I) ~~–~~there ~~is~~ is ~~no significant~~little $^1O_2$~~-signal~~ before ~~light excitation~~illumination both in original and photodegraded samples; (II) ~~–(the red curve in Fig.7A (I)) and only a small amount of~~ $^1O_2$ are generated both in original and photodegraded samples after 60 min in dark and the content of $^1O_2$ in original samples is higher than that in photodegraded samples~~is generated after 60 min in dark (the red curve in **Fig.7A (II)**)~~, which suggest POA could generate $^1O_2$ without illumination; (III) As expected, compared with the samples without illumination, ~~, which indicated that POA has certain oxidability. As expected, compared with the samples without light excitation (the red curve in **Fig. 7A (I)**),~~ the ~~signal intensity~~content of $^1O_2$ increases by ~~a factor of~~ 3 times both in original and photodegraded samples; after 60 minutes of illumination. Consistent with (II), the content of $^1O_2$ in original samples is also higher than that in photodegraded samples (42.1%), ~~light excitation (the red curve in **Fig. 7A (III)**),~~ which prove the inhibiting ~~significant promoting~~ effect~~-of light on~~ of COM photodegradation on $^1O_2$~~.~~; (IV) ~~–~~However, the content of $^1O_2$ is not reduced when the triplet state is quenched by sorbic acid~~-(the red curve in **Fig.7A (IV)**)~~. Sorbic acid is a ~~trapping~~capturing agent ~~of~~ for high-energy triplet state (triplet energies E_T = 239-247 kJ/mol) (Zhou et al., 2019; Moor et al., 2019)~~,~~. T~~t~~herefore, 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 photochemical characteristics of ambient PM are different from POA.~~~~The ~~In ambient PM~~COM photo-degradation can change the yield of 1O2.~~,~~ Compared with original POA samples,~~ (V) the content of $^1O_2$ in original and photodegraded samples is similar to POA; (VI) Compared with (V), the content of $^1O_2$ almost unchanged after 60 min in dark, which is opposite to POA. The result suggests ambient PM could not generate $^1O_2$ without illumination. (VII) The content of $^1O_2$ increases significantly after 60 minutes of illumination and the content of $^1O_2$ in original samples is higher than that in photodegraded samples (41.0%). (VIII) When the triplet state is quenched by sorbic acid, the signal of $^1O_2$ disappears. The result suggests that $^1O_2$ is mainly generated by high-energy ^{3}COM* in ambient PM. The above results show that the precursor of high-energy triplet state could be photodegraded, which directly lead to the decrease in $^1O_2$ in ambient PM. In summary, a decrease in the yield of $^1O_2$ because ~~the signal intensity of 1O2 decreases significantly in the samples with 7 days of photolysis (the blue curve in Fig.7A), with an average decrease of 42.1% (Fig.7C), which prove that photo-degradation has a attenuating effect on the photochemical activity. Similar to the original sample, in the photolyzed samples, the signal intensity of 1O2 does not decrease obviously when the high-energy triplet states are quenched by sorbic acid. The mechanism is the same as the original samples. The results also reveal that COM photo-degradation do not change the mechanism of low-energy 3COM* inducing 1O2 in POA.~~

~~The photochemical characteristics of ambient PM are different from POA.~~ ~~More narrowly, there is no obvious 1O2 signal in original ambient PM samples before light excitation (the red curve in Fig.7B (I)). 1O2 is also not generated after 60 min in dark (the red curve in Fig.7B (II)). The content of 1O2 increase significantly after 60 minutes of light excitation (the red curve in Fig.7B (III)). When the triplet states are quenched by sorbic acid (Fig.7B (IV)), the signal of 1O2 disappears. The result suggests that 1O2 is mainly induced by high-energy 3COM* in ambient PM. Compared with the original samples, the signal intensity of 1O2 decrease by 41.0% on average in photolyzed samples (the red curve in Fig.6B). T~~th~~is~~e~~ characteristic suggests the attenuating ~~inhibiting effect of COM photo-degradation on photochemical activity in ambient PM~~, which is similar to ~~ and POA and COM photodegradation do not change the mechanism of low-energy ^{3}COM* generating $^1O_2$ in POA~~.~~. However, the quenching effects of sorbic acid ~~on~~ in ~~various~~ POA and ambient PM ~~aerosols~~ are different because of the difference in ^{3}COM* energy~~ (Fig.7 (IV))~~. ~~The above results directly show that the precursor of high-energy triplet states could be photolyzed, which directly lead to the decrease of 1O2 yield in the ambient PM. Other experiments are needed to study whether the low-energy triplet precursors in POA are photolyzed and cause a decrease in the yield of 1O2.~~



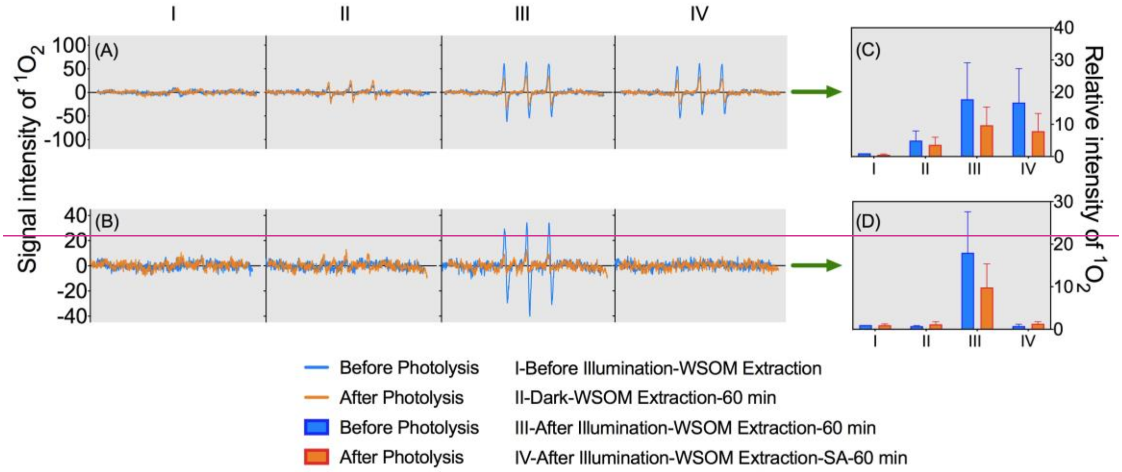


Fig.~~7~~ 5 ~~Variations~~ Changes in ~~of~~ DOM ~~inducing~~ generating $^1O_2$ before and after ~~photolysis~~photodegradation. (A) POA; (B) Ambient POA. ~~(A) and (C) are the results obtained from POA samples. (B) and (D) are the results obtained from Ambient PM. The left of the figure was the EPR 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~~ in COM photo-degradation~~, changes in optical properties and chemical compositions, –~~ and the effect of COM photo-degradation on ~~–~~optical properties, chemical compositions, and photochemical activity ~~and aerosol aging~~. The ~~properties~~ characteristics of COM photo-degradation were revealed. COM photo~~-~~degradation could ~~be explained~~result in ~~by~~ reduction of carbonaceous components, attenuation~~decrease of –~~ of ~~light absorption~~optical ~~capacity~~properties, and ~~attenuation of~~changes in components~~ fluorescence intensity~~. We also propose that the COM photodegradation should be evaluated from the three aspects for further study. (1) The impact of COM photodegradation on carbonaceous content are unclear. Previous studies have revealed that WSOC did not significantly change in the river DOM (Gonsior et al., 2009) and 0.2% of DOC was mineralized (Tranvik et al., 1998). However, the observation in the study suggests that changes in carbonaceous component is different in aerosols, which could be attributed to the differences in original components. ~~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.~~ (2) Decreasing in optical properties is significant. Absorption coefficient and fluorescence intensity can be thought of as a tracer for molecular weight (Stewart & Wetzel, 1980). Therefore, optical properties could indicate the changes in molecular weight of COM during the photodegradation process. The characteristic could be suitable for exploring the impact of photodegradation on COM components. (3) ~~We studied that the p~~Photo~~-~~degradation~~ could lead to~~ of COM~~ decompose~~ may dominant ~~and change in types~~the fluorophores components (Aiona et al., 2018; Timko et al., 2015). High-molecular-weight ~~DOM~~ COM could be decomposed into low-molecular-weight ~~DOM~~ COM during ~~photolysis~~photodegradation process. 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~~ C~~attenuation and type conversion of~~hanges in COM may ~~prov~~re~~ide an important basis to trace the aerosol aging process.~~ present the degree of organic substances oxidation. Therefore, we suggested that optical parameter and degree of oxidation of organic molecules should be use for characterizing the aerosol photo-aging process (Maizel et al., 2017). ~~Optical properties were also affected by COM photo-degradation.~~

~~The effects of COM photo-degradation on the photochemical activity in aerosols are studied.~~ Photodegradation~~Aerosol aging~~ can not only change the ~~type and content~~properties and components of COM, but also change their photochemical activity, which furtherly has a potential impact on the aerosol fate. Photodegradation and/or conversion of COM could be considered to be the main influence factor for photochemical reaction capacity (McNight et al., 2001; Zepp et al., 1985). .~~We evaluated the effect of COM photo-degradation on the photochemical activity.~~ Photochemical activity was quantified ~~The ability of~~ by the yield of triplet state~~ generation~~ and $^1O_2$~~ yield was chosen to quantify the photochemical activity~~. ~~–~~However, two different methods, two different results. COM photodegradation can restrain $^1O_2$ generation but the effect of photodegradation on ^{3}COM* are unclear. Photodegradation has a significant inhibiting effect on the $^1O_2$ yield in aerosols (Latch et al. 2006; Chen et al., 2018). We insist that aerosol aging would be changed by photodegradation due to the yield of $^1O_2$ is changed. Changes in triplet state generation are uncertain in ambient PM and POA. There are two reasons for it. ~~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~~ COM ~~could generate~~are the precursor of ^{3}COM* in aerosols.~~Triplet state generation ability remain unchanged in ambient PM and increased in POA~~ On the other hand, the energy of capturing agents was closely related to ^{3}COM* quantification and ^{3}COM* could not be captured completely. Other capturing agents may lead to different results.~~ during aerosol aging.~~ ~~Thus,~~ Thus, ^{3}COM* could not properly illustrate~~COM~~ photo-degradation~~ could not properly illustrate changes in ^{3}COM*~~. COM photodegradation would be play an important role in the content of ROS and ROS could celebrate the COM photooxidation (Claeys et al., 2004). Given the results, the interaction effect is significant in aerosol. ~~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.~~

In summary, atmospheric photochemistry process has a remarkable impact on aerosol aging. Prediction of atmospheric lifetime and improvement of quality are strongly associated with photochemistry. We prove that ~~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~~carbonaceous content, absorption coefficients, fluorescence intensity, and photochemical activities are~~ in aerosols. It may be more~~ useful to reflect COM photodegradation process and aerosol fate. In addition, COM photodegradation have different impact on chemical activity in different aerosols, which may have different mechanisms. Therefore,~~ distinguish the types of ^{3}COM* into high and low energies, so that~~ the mechanisms of COM photodegradation effecting ~~the mechanism of COM photochemical reaction can be elucidated. Different types of aerosols have different aging mechanisms, so the environmental impacts caused by COM should also be different.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.~~aerosol photo-aging deserve further investigation.

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−S5, Figures S1−~~S8~~S10, 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.

Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; Jenkin, M. E.; Rossi, M. J.; Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II - gas phase reactions of organic species, Atmos. Chem. Phys., 6, 3625-4055, http://dx.doi.org/10.5194/acp-6-3625-2006, 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.

Budisulistiorini, S. H.; Riva, M.; Williams, M.; Chen, J.; Itoh, M.; Surratt, J. D.; Kuwata, M.: Light-Absorbing Brown Carbon Aerosol Constituents from Combustion of Indonesian Peat and Biomass. *Environ. Sci. Technol.*, *51*, 4415-4423, http://dx.doi.org/10.1021/acs.est.7b00397, 2017.

Canonica, S.; Hellrung, B.; Müller, P.; Wirz, J.: Aqueous Oxidation of Phenylurea Herbicides by Triplet Aromatic Ketones, Environ. Sci. Tech., 40, 6636-6641, https://doi.org/10.1021/es0611238, 2006.

Carlton, A. G.; Turpin, B. J.; Altieri, K. E.; Seitzinger, S.; Reff, A.; Lim, H. J.; Ervens, B.: Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous photooxidation experiments, Atmos. Environ., 41, 7588-7602, http://dx.doi.org/10.1016/j.atmosenv.2007.05.035, 2007.

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. 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, 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, Q.; Mu, Z.; Xu, L.; Wang, M.; Wang, J.; Shan, M.; Fan, X.; Song, J.; Wang, Y.; Lin, P.; Du, L.: Triplet-state organic matter in atmospheric aerosols: Formation characteristics and potential effects on aerosol aging, Atmos. Environ., 252, 118343, https://doi.org/10.1016/j.atmosenv.2021.118343, 2021.

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.~~Claeys, M.; Graham, B.; Vas, G.; Wang, W.; Vermeylen, R.; Pashynska, V.; Cafmeyer, J.; Guyon, P.; Andreae, M. O.; Artaxo, P.; Maenhaut, W.: Formation of secondary organic aerosols through photooxidation of isoprene, Science, 303, 1173-1176, http://dx.doi.org/10.1126/science.1092805, 2004.

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.

Encinas, M. V.; Lissi, E. A.; Olea, A. F.: Quenching of triplet benzophenone by vitamins E and C and by sulfur containing amino acids and peptides, Photochem. Photobiol., 42, 347-52, http://dx.doi.org/10.1111/j.1751-1097.1985.tb01580.x, 1985.

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.

George, C.; Ammann, M.; D'Anna, B.; Donaldson, D. J.; Nizkorodov, S. A.: Heterogeneous Photochemistry in the Atmosphere. Chem. Rev., 115, 4218-4258, 10.1021/cr500648z, 2015.

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.

Jo, D. S.; Park, R. J.; Lee, S.; Kim, S. W.; Zhang, X.: A global simulation of brown carbon: implications for photochemistry and direct radiative effect, Atmos. Chem. Phys., 16, 3413-3432, http://dx.doi.org/10.5194/acp-16-3413-2016, 2016.

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.~~Mang, S. A.; Henricksen, D. K.; Bateman, A. P.; Andersen, M. P. S.; Blake, D. R.; Nizkorodov, S. A.: Contribution of Carbonyl Photochemistry to Aging of Atmospheric Secondary Organic Aerosol, J. Phys. Chem. A, 112, 8337-8344, http://dx.doi.org/10.1021/jp804376c, 2008.

Marciniak, B.; Bobrowski, K.; Hug, G. L.: Quenching of triplet states of aromatic ketones by sulfur-containing amino acids in solution. Evidence for electron transfer, J. Phys. Chem., 97, 11937-11943, 10.1021/j100148a015, 1993.

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.

Nebbioso, A.; Piccolo, A.: Molecular characterization of dissolved organic matter (DOM): a critical review, Anal. Bioanal., Chem. 405, 109-124, http://dx.doi.org/10.1007/s00216-012-6363-2, 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 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.~~Stewart, A. J.; Wetzel, R. G: Fluorescence: absorbance ratios—a molecular-weight tracer of dissolved organic matter, Limnol. Oceanogr., 25, 559-564, https://doi.org/10.4319/lo.1980.25.3.0559, 1980.

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, 2020a.

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, 2020b.

Timko, S.; Maydanov, A.; Pittelli, S.; Conte, M.; Cooper, W.; Koch, B.; Schmitt-Kopplin, P.; Gonsior, M.: Depth-dependent photodegradation of marine dissolved organic matter, Front. Mar. Sci., 2, https://doi.org/10.3389/fmars.2015.00066, 2015.

Tranvik, L.; Kokalj, S.: Decreased biodegradability of algal DOC due to interactive effects of UV radiation and humic matter, Aquat. Microb. Ecol., 14, 301-307, https://doi.org/10.3354/ame014301, 1998.

~~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.~~Wawzonek, S.; Laitinen, H. A.: The Reduction of Unsaturated Hydrocarbons at the Dropping Mercury Electrode. II. Aromatic Polynuclear Hydrocarbons, J. Am. Chem. Soc., 64, 2365-2368, http://dx.doi.org/10.1021/ja01262a040, 1942.

~~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.

Xu, W.; Gao, Q.; He, C.; Shi, Q.; Hou, Z.-Q.; Zhao, H.-Z.: Using ESI FT-ICR MS to Characterize Dissolved Organic Matter in Salt Lakes with Different Salinity, Environ. Sci. Technol., 54, 12929-12937, http://dx.doi.org/10.1021/acs.est.0c01681, 2020.

Yang, X. M.; Yuan, J.; Yue, F. J.; Li, S. L.; Wang, B. L.; Mohinuzzaman, M.; Liu, Y. J.; Senesi, N.; Lao, X. Y.; Li, L. L.; Liu, C. Q.; Ellam, R. M.; Vione, D.; Mostofa, K. M. G.: New insights into mechanisms of sunlight- and dark-mediated high-temperature accelerated diurnal production-degradation of fluorescent DOM in lake waters, Sci. Total Environ., 760, 14, http://dx.doi.org/10.1016/j.scitotenv.2020.143377, 2021.

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.

Zhao, Y.; Hallar, A. G.; Mazzoleni, L. R: Atmospheric organic matter in clouds: exact masses and molecular formula identification using ultrahigh-resolution FT-ICR mass spectrometry, Atmos. Chem. Phys., 13, 12343-12362. http://dx.doi.org/10.5194/acp-13-12343-2013, 2013.

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.