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

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Abstract: Atmospheric chromophoric organic matter (COM) ~~can participate~~plays a fundamental role in ~~photochemical reactions because of the photosensitivity, thus COM has a potential contribution to aerosols aging~~photochemistry and aerosol aging. However, the ~~effect~~effects of ~~COM~~ photodegradation on chemical components and photochemical reactivity ~~and aerosol aging~~of COM are ~~not fully understood.~~remain unresolved. Here, we report the potential impacts of photodegradation on ~~carbonaceous components~~carbon content, optical ~~properties, fluorophores components~~property, fluorophore component, and photochemical reactivity~~. We confirm that both~~ of organic aerosols. After 7 days of photodegradation, fluorescent intensity and absorption coefficient of water-soluble and ~~water-insoluble COM are photodegraded, and fluorescent intensities~~ methanol-soluble COM decrease by ~~70~~71.4% and 32.0% on average~~. Furthermore, low~~, respectively. Low oxidation humic-like substance (HULIS) is converted into high oxidation HULIS due to photooxidation, the result suggests that ~~oxidation of HULIS can be used to trace~~the chromophore composition has changed as well as the degree of ~~aerosols~~aerosol aging. COM ~~Photodegradation~~photodegradation has a significant impact on photochemical reactivity. The ~~content~~generation rate constants of triplet state COM ~~decreases~~ (^{3}COM*) decrease slightly in ambient particulate matter (ambient PM) but ~~increases~~increase in primary organic aerosol (POA) following photodegradation. The ~~result~~results highlight that ~~photodegradation has~~ the opposite effect ~~on different aerosols as a result of the changes~~of photodegradation on photochemical reactivity in ~~components.~~POA and ambient PM. The ability of COM generating singlet oxygen ~~declines~~ ($^1O_2$) decreases obviously, which ~~is consistent with optical properties. Photodegradation of~~could be attributed to photodegradation of chromophoric precursors ~~limit singlet oxygen generation and affect~~of $^1O_2$. The combination of optical property, chemical component, and reactive oxygen species have an important impact on the ~~aerosol photochemistry process. In conclusion, COM photodegradation not only change the compositions and properties, but also change~~atmosphere quality. The new insights on photodegradation of COM in aerosol ~~aging.~~reinforce the importance of studying DOM related with the photochemistry and aerosol aging.

Key word: atmospheric ~~chromophores~~chromophore; photodegradation; EEMs; triplet state; reactive oxygen species.

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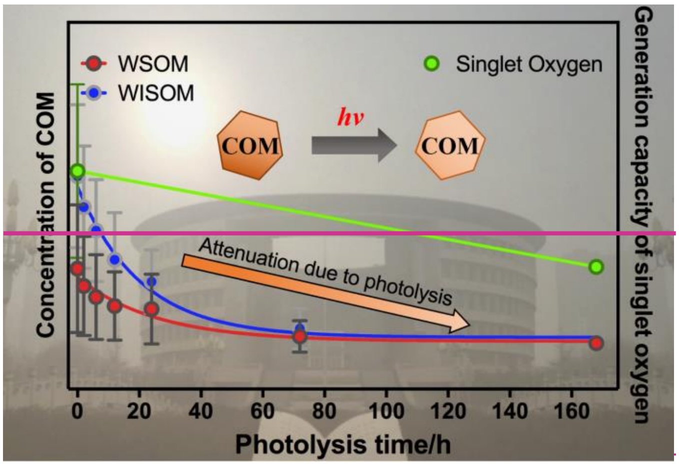
WSOM
WISOM
Singlet Oxygen
COM
hv
COM
Attenuation due to photolysis
Concentration of COM
Generation capacity of singlet oxygen
0
20
40
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80
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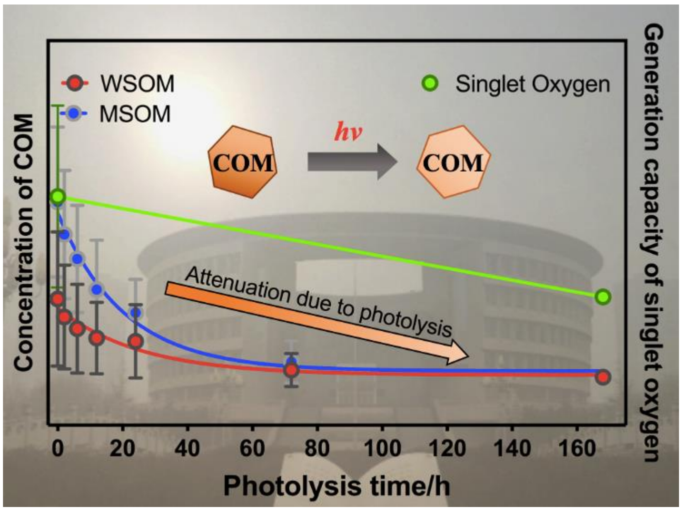
Photolysis time/h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1. Introduction

Atmospheric chromophoric organic matter (COM) mainly ~~originate~~originates from biomass combustion ~~emissions~~emission and secondary ~~aerosols~~organic aerosol (SOA) (Andreae & Gelencser, 2006; Budisulistiorini et al., 2017; Graber & Rudich, 2005; Zappoli et al., 1999). Because of the significant absorption for short-wave radiation (Wavelength range from near-ultraviolet light to visible light) (Rosario-Ortiz and Canonica, 2016; Cheng et al., 2016), COM may undergo photochemical ~~process~~processing and have a significant impact on atmospheric components and quality (Zhao et al., 2013; Jo et al., 2016). Therefore, simulation and evaluation of COM photochemistry ~~is~~are necessary for understanding aerosol aging.

As photosensitive substances, the optical properties and components of COM change significantly under solar irradiation (Alkinson et al., 2016; Carlton et al., 2007; Lee et al., 2013; Murphy et al., 2013). On the one hand, optical properties change significantly that due to ~~chromophores are~~COM is photo-~~bleached~~bleaching in ~~aerosols. For example, Lee et al.~~aerosol. Zhong and Jang (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 organic matter (OM~~. The reason~~) was ~~the major components of wood-burning OM~~bleaching, such as conjugated aromatic rings and phenols, and ~~hydroxyl groups, could be photodegraded.~~hydroxylated aromatic phenols; Lee et al. (2014) also reported that the MAC of secondary organic aerosol (SOA) continued to decrease in the UV-Vis spectral. On the other hand, photodegradation has a significant effect on the ~~composition~~chemical components of COM. ~~Photodegradation~~COM can ~~cause that COM decompose~~be decomposed into small molecules ~~and~~after photodegradation and the photodegraded COM may have lower volatility and higher oxidation degree ~~after photodegradation~~ (Grieshop et al., 2009). COM could also be generated through the photochemical processes, which could be attributed to the formation of SOA~~ during the photochemical reaction process.~~. For example, ~~Oligomeric~~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~~were 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 primary organic aerosol (POA) in the short-wavelength visible and near-UV region (Zhong & Jang, 2014; Saleh et al., 2013; Harrison et al., ~~.~~2020). As a result, ~~photochemical process may play~~photodegradation plays an important role in the components and properties of COM~~. Changes in chemical composition~~ and ~~optical properties also have a significant impact on~~thereby change photochemical activity~~ in turn~~. There are limited studies that ~~comprehensive~~comprehensively exploring the ~~components and properties transformation~~characteristics of photodegradation of COM in ~~aerosols during the photodegradation processes~~aerosol.

~~Atmospheric~~Photochemical process of COM ~~could participate in the complex photochemical reaction, which further affect~~largely determines the aerosol aging (Mang et al., 2008). On the one hand, COM ~~participates~~is often used as reactant in ~~atmospheric~~ photochemical processes ~~as a reactant.~~in aerosol. For example, COM ~~can~~could be oxidized by hydroxyl radicals (•OH~~) (Zhao et al., 2015) and the~~). The formation of polyols can be attributed to photooxidation of isoprene, which could be initiated by •OH (Claeys et al., 2004~~).~~; Zhao et al., 2015). Humic-like substance (HULIS) with complex functional groups has significant contribution to photochemistry (George et al., 2015; Nebbioso & Piccolo, 2013; Wenk et al., 2013). On the other hand, COM also participates in atmospheric photochemistry process indirectly through generating reactive intermediates~~.~~, energy transferring, and involving electron. Upon light ~~absorption~~exposure, high-energy singlet state COM (^{1}COM*) could be ~~generated~~excited. ^{1}COM* ~~deactivate quickly with the ways of~~deactivates by emitting photon (fluorescence) and intersystem crossing (triplet state~~, ~~ (^{3}COM~~*). ^{3}COM*~~*) generation). ^{3}COM* not only can produce photochemical reaction directly, but also can generate reactive oxygen species (ROS), such as singlet oxygen (${}^1O_2$), super oxide (•O_2^-~~)~~$^-$), and •OH, which ~~indicate~~indicates that ^{3}COM* ~~play~~plays 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~~COM, such as aromatic ketones (Canonica et al., 2006; Marciniak et al., 1993), benzophenone (Encinas et al., 1985), and phenanthrene (Wawzonek & Laitinen, 1942), have been identified as the ~~precursor~~precursors of ^{3}COM*. ~~Probes~~Chemical probes, such as 2,4,6-trimethylphenol (TMP) and sorbic acid (SA), are applicable to evaluate the ~~chemical reactivity (~~productivity of ^{3}COM* (Zhou et al., 2019; Moor et al., 2019; Chen et al., 2021). ~~Why ^{3}COM* is employed not~~Compared with ^{1}COM~~*? The reasons~~*, the characteristics of ^{3}COM* are lower formation rate (15~~–~~~100 times slower than ^{1}COM*), lower quenching rate (20000 times lower than ^{1}COM*), and ~~highter~~higher steady-state ~~concentrations of ^{3}COM* (~~concentration (200~1300 times higher than ^{1}COM*) (McNeil et al., 2016). Therefore, the reaction rate constant of ^{3}COM* is used in evaluating the photochemical reactivity. Considering the potential effect of ~~COM~~ROS on aerosol aging and atmospheric quality, it is necessary to clarify the path and mechanism.

COM photochemistry may dominate the chemical composition and the aerosol aging process. In order to illustrate the properties of COM photodegradation and the effect of COM photodegradation on aerosol aging, we simulate the process of COM photodegradation and COM generating ROS in the laboratory. The objectives of the study are (1) to clarify the variation characteristics of ~~carbonaceous components variation~~ carbon content during the COM photodegradation process, (2) to explore the effects of ~~photo-degradation~~photodegradation on ~~the~~ fluorophores and optical properties ~~of~~in water-soluble and ~~water-insoluble chromophores~~methanol-soluble COM, and (3) to investigate the ~~effects~~effect of COM photodegradation on photochemical reactivity ~~and aerosol aging~~ (photochemical reactivity is characterized by the generation capacity of triplet state and singlet oxygen ~~generation capacity~~).

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 location ~~is~~was about 30 m). 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 ℃ prior to use.

The POA samples were collected through a combustion chamber. Straw and coal burning ~~are~~were the main way of heating and cooking in the rural areas in China. Therefore, wheat straw-, corn straw-, rice straw~~-~~, and wood-burning samples were collected (Schematic ~~diagrams~~diagram of ~~combustion equipment~~combustion chamber is shown in **Figure S1**). The POA samples were stored in the refrigerator at -20 ℃ prior to use.

2.2 Photodegradation experiment

A quartz reactor was designed for ~~photolysis~~photodegradation 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 ~~illumination~~photodegradation times were 0 h, 2 h, 6 h, 12 h, 24 h, 3 d and 7 d~~, respectively. Two capsules (**Figure S2(b) & (c)**)~~ and a series of photodegraded samples were ~~designed for triplet state and ROS generation experiment.~~collected.

~~*2.3 Carbonaceous components analysis*~~

2.3 Carbon content measurement

The original and ~~photolyzed~~photodegraded samples were ultrasonic extracted with ultrapure water (>18.2 MΩ•cm~~, Master series~~, Hitech, China) and filtered through a 0.45 μm filter (Jinteng, China) to obtain the water-soluble organic matter (WSOM). After water extraction, ~~the extracted filters~~residual organic matter were further extracted with methanol (HPLC Grade, Fisher Chemical, America) and filtered through a 0.45 μm filter to obtain ~~water-insoluble~~methanol-soluble organic matter (~~WISOM~~MSOM). The blank samples were also extracted with the same method.

The ~~analytical~~measurement method of ~~carbonaceous components~~carbon content has been described previously (Mu et al., 2019). Briefly, 100 μL ~~extracts were~~extract was injected on the baked quartz filter. Then, the wet ~~filters were~~filter was dried out by a rotary evaporator and the dried ~~filters were~~filter was analyzed by the OC/EC online analyzer (Model 4, Sunset, America) with the approach of NIOSH 870 protocol (Karanasiou et al., 2015). Organic carbon (OC) was measured in the absence of oxygen. An oven in the instrument was filled with helium and temperature was risen in a gradient style. Different temperatures are needed for particular analysis phases (OC1-310 ℃, OC2-472 ℃, OC3-615, OC4-850 ℃). Element carbon (EC) was measured in the present of oxygen. The oven in the instrument was filled with helium-oxygen gas mixture ($He/O_2 = 9/1$). Different temperatures were also needed for particular analysis phases (EC1-550 ℃, EC2-625 ℃, EC3-700℃, EC4-775 °C, EC5-850 °C, EC6-870 °C). The products in the heating process were further oxidized to CO_2. The carbon content was obtained through the measurement of CO_2. Six parallel samples were analyzed and the uncertainty of the method was <3.7% (one standard deviation).

2.4 Optical analysis

The light absorption and EEM spectra of ~~the extracts~~WSOM and MSOM were measured by an Aqualog fluorescence spectrophotometer (Horiba Scientific, America). The range of excitation wavelength was 200-600 nm ~~and the~~with an interval of 5 nm. The range of emission wavelength was 250-800 nm. ~~The interval was 5 nm.~~ The ~~exposure~~integration time was 0.5 s. The absorption spectra ~~were~~was also recorded in the wavelength range of 200-600 nm. Water and methanol ~~background~~blank samples were measured using the same method and the ~~background signals were~~blank value was subtracted from the sample ~~signals~~value. 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~~ parallel factor analysis model (PARAFAC~~ model~~) to identify fluorophores (The ~~detailed analysis process refers~~model referred to the previous papers~~,~~ (Murphy et al., 2013; Chen et al., 2016a; Chen et al., 2016b)). WSOM and ~~WISOM~~MSOM (111 samples) were combined in the dataset to create the PARAFC model. 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~~fluorescent components were identified (Error analysis of the models ~~are~~is shown in **Figure S4** of SI).

2.5 Triplet state generation experiment

As short-lived reactive intermediates, ^{3}COM* ~~have~~has an important impact on photochemical process in atmospheric environment (Kaur et al., 2018). Therefore, changes in ^{3}COM* generation ability before and after photodegradation were studied. ~~Chemical probe 2,4,6-trimethylphenol (~~The samples with the photodegradation time of 0 and 7 d were defined as the original and photolyzed samples, respectively. Only WSOM of original and photolyzed samples was used in the triplet state generation experiment. A capsule (**Figure S2(c)**) was designed for this experiment. TMP~~)~~ was used as the capturing agent for the ~~triplet state.~~^{3}COM*. 60 μL of WSOM ~~extracts (WSOC concentrations are~~extract (Carbon content is shown in **Table S3**) and 60 μL of TMP solution (c_{TMP} = 20 μM, Aladdin, China) were mixed in the capsule~~ (**Figure S2(b)**).~~. The capsule was placed in the reactor (**Figure S2(a)**). The~~ illumination~~ times ~~was~~of optical excitation were 0, 5, 10, 15, 30, 45, 60 and 90 min, respectively. Then 90 μL mixed solution was taken out from the capsule at different time points and 30 μL of phenol solution (c_{phenol} = 50 μM, Aladdin, China) ~~were~~was added into the mixed solution (Phenol solution was used as the internal standard substance for TMP quantification).

TMP was ~~quantified~~measured by liquid chromatography (LC). The method ~~of LC are~~was 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~~was 14.5 min. Kaur & Anastasio (2018) and Richards-Henderson et al. (2015) have reported that TMP consumption ~~conform~~conformed to first-order kinetics. The ~~first-order kinetic equation~~curvy fitting was ~~used to~~

~~fit~~performed by exponential ~~relationship~~function among the TMP concentration (c_{TMP}/μM), the ~~illumination~~optical excitation time (t/min) and triplet state generation rate ~~constants~~constant (k_{TMP}/min^{-1}):

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

2.6 Singlet oxygen generation experiment

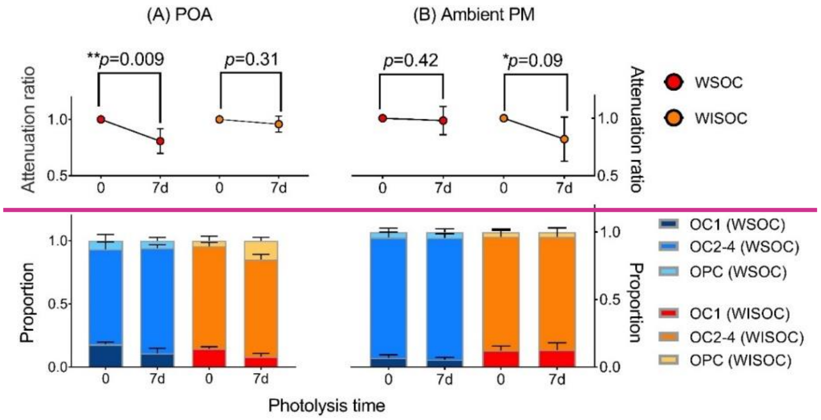
The ~~effects~~effect of ~~the~~ COM photodegradation on singlet oxygen ~~were~~was studied. A capsule (**Figure S2(b)**) was designed for $^{1}O_2$ generation experiment. Only WSOM of original and photolyzed was used in the singlet oxygen generation experiment. 4-Hydroxy-2, 2, 6, 6-tetramethylpiperidine (TEMP, c_{TEMP}=240 mM, Aladdin, China) was used as the capturing agent for ~~singlet oxygen~~$^{1}O_2$ and ~~captured singlet oxygen~~$^{1}O_2$ was ~~quantified~~measured by EPR spectrometer (MS5000, Freiberg, Germany). ~~Sorbic acid (~~SA~~, C_{SA}~~ (c_{SA}=133.3 μM, Aladdin, China) was used as quenching agent for ~~triplet state.~~^{3}COM*. The method was as follows: (1) $^{1}O_2$ was measured before optical excitation. 40 μL WSOM, 40 μL TEMP, and 40 μL ultra-pure water were mixed in the capsule (**Figure S2(~~c~~b)**). Then, 50 μL of the mixed solution was taken out by capillary for EPR analysis; (2) $^{1}O_2$ was measured without optical excitation after 60 min. 40 μL WSOM, 40 μL TEMP and 40 μL ultra-pure water were mixed in the capsule. The capsule was placed in the reactor for 60 min without illumination. Then 50 μL mixed solution was taken out by capillary for EPR analysis; (3) $^{1}O_2$ was measured after 60 min of optical excitation. 40 μL WSOM, 40 μL TEMP and 40 μL ultra-pure water were mixed in the capsule. The capsule was illuminated in the reactor for 60 min. 50 μL mixed solution was taken out by capillary for EPR analysis; (4) ^{3}COM* was quenched and $^{1}O_2$ was measured after 60 min of optical excitation. 40 μL WSOM, 40 μL TEMP and 40 μL SA solution were mixed~~. The~~ in capsule. The mixed sample was illuminated in the reactor for 60 min, then 50 μL mixed solution was taken out by capillary for EPR analysis.

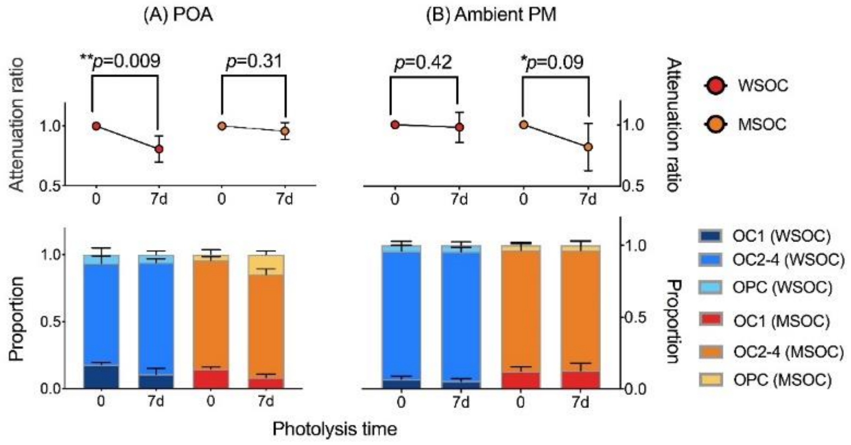
3. Results and discussion

3.1 Effect of COM photodegradation on ~~carbonaceous components~~carbon content

~~COM can be decomposed and transformed in aerosol due to photodegradation~~ **Figure** ~~(Wong et al., 2015).~~ ~~**Fig.**~~**1** describes the changes in ~~the~~carbon content ~~of carbonaceous components~~ before and after COM photodegradation. In POA~~,~~ (**Figure 1(A)**), water~~—~~-soluble and ~~water insoluble~~methanol-soluble organic carbon (WSOC and ~~WISOC~~MSOC) decrease by 22.1% and 3.5%, respectively. The results suggest that WSOC tend to be photodegraded in POA. ~~As shown in **Fig.1(A)**,~~In WSOC, 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~~) and OC with ~~small molecular weight and highly volatile~~these characteristics tend to be photodegraded. In ~~WISOC~~MSOC, there is a process of OC1 translating into pyrolysis carbon (OPC). The proportion of OPC in ~~WISOM show~~MSOC shows an increasing trend (an average increase of 2.4 times). ~~The pyrolysis~~Pyrolysis carbon is identified as oxygen-containing organic substance. Thus, the increasing oxygen-containing organic matter may be due to the photo-inducing oxidation reaction.

POA is fresh and ambient PM ~~have~~has undergone long-term aerosol aging. In ambient PM (~~Fig.1B),~~**Figure 1(B)**), WSOC is nearly unchanged and ~~WISOC~~MSOC decreases by 18.2%, which is ~~opposite~~in contrast to POA. The results reflect that ~~WSOC~~OM has been photodegraded ~~completely~~adequately following the photodegradation and mineralization process in WSOM of ambient PM. However, ~~WISOC~~MSOC with high molecular weight could not be photodegraded ~~completely~~adequately and thereby continue to be photodegraded in laboratory. The proportions of OC1, OC2-4, and OPC are relatively stable in ambient PM, which ~~indicate~~indicates that the decreasing ~~proportion~~proportions in the different ~~stage~~stages are similar and the tendency is also ~~opposite~~in contrast to POA. The result reflects that different ~~carbonaceous components~~molecular weight OM may have the similar abilities of photodegradation in ambient PM. ~~Organic matter with high molecular weight is photocomposed to small~~The proportion of different molecular weight ~~and the molecular weight tend to be consistent~~OM is nearly unchanged following the photodegradation~~.~~ in ambient PM.





~~Fig.~~

Figure 1 Changes in ~~carbonaceous components~~carbon content before and after 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 photodegradation on optical properties

As shown in ~~**Fig.**~~**Figure 2**, both absorption ~~coefficients~~coefficient and total fluorescence volume (TFV, RU-nm^2/m^3) significantly decrease following ~~aerosol~~ photodegradation, which ~~suggest~~suggests that COM ~~are~~is photo-~~bleached~~bleaching (Aiona et al., 2018; Duarte et al., 2005; Liu et al., 2016). The attenuations of fluorescence intensity and absorption ~~coefficients~~coefficient are ~~fit~~fitted to first-order decay. The absorption ~~coefficients decrease~~coefficient decreases by 32.0% and TFV decreases by 71.4% on average. However, as shown in ~~**Fig.**~~**Figure 3**, fluorescence intensities increase and decrease in different regions of EEMs (Aiona et al., 2018; Timko et al., 2015).

~~In POA (**Fig.2(B)**), TFV decreases by 74.8% on average and the attenuation are fitted with first-order decay kinetics. 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). Changes in fluorescence intensities may also depend on the types and water-insoluble wood-burning COM are difficultly photodegraded. In addition, fluorophores photodegradation depend~~

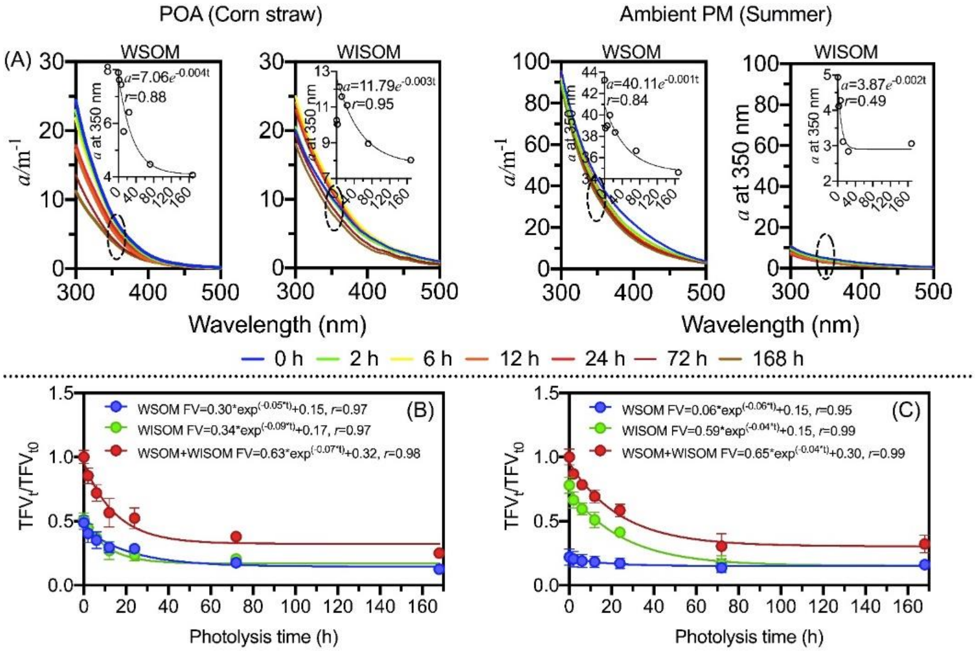
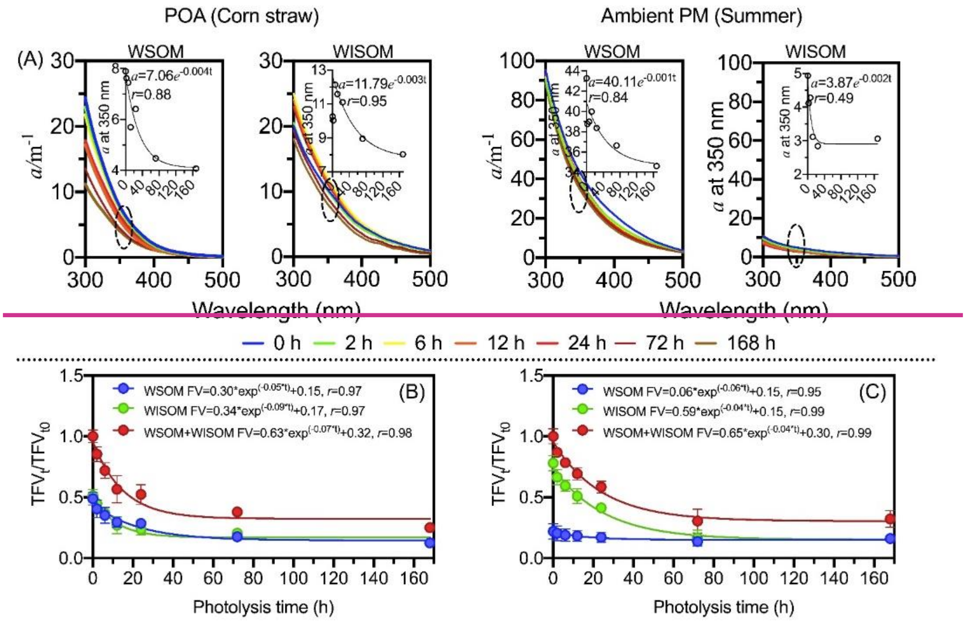


Figure 2 Changes in absorption coefficient~~on the photochemical environment, such as solution pH (Aiona et al., 2018), salinity (Xu et al., 2020), and temperature (Yang et al., 2021).~~

~~In ambient PM (**Fig.2(C)**), the decay rate constant of TFV in ambient PM (k = 0.04 h^{-1}) is lower than in POA (k = 0.07 h^{-1}). TFV of water-soluble fluorophores decreases by 79.4% but water-~~

~~soluble fluorophores decreases by 26.7%. 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.~~



~~**Fig.2** Changes in light absorption~~ and fluorescence volume during the photodegradation process. (A) Absorption coefficient. The scatter plot is absorption coefficient at 350 nm. (B) and (C) the attenuation curve of fluorescence volume in POA (except for the wood sample) and ambient PM, respectively.

In POA (**Figure 2(B)**), TFV decreases by 74.8% on average and the exponential curve method was used to analysis the attenuation of fluorescence intensity. The attenuation of TFV are significant similarities between WSOM and MSOM. However, wood-burning samples are distinct from other POA samples, TFV of wood-burning COM only decreases by 9.0% and fluorescence volume of MSOM of wood-burning samples remain almost unchanged (**Figure S7**). There are two main reasons. On the one hand, methanol-soluble secondary OM is generated slightly in wood-burning samples (Zhong & Jang, 2014). On the other hand, methanol-soluble wood-burning COM is difficultly photodegraded. In addition, fluorophores photodegradation also depends on the photochemical environment, such as solution pH (Aiona et al., 2018), salinity (Xu et al., 2020), and temperature (Yang et al., 2021). Therefore, we suppose that photodegradation of wood-burning COM may largely depend on photodegradation environment.

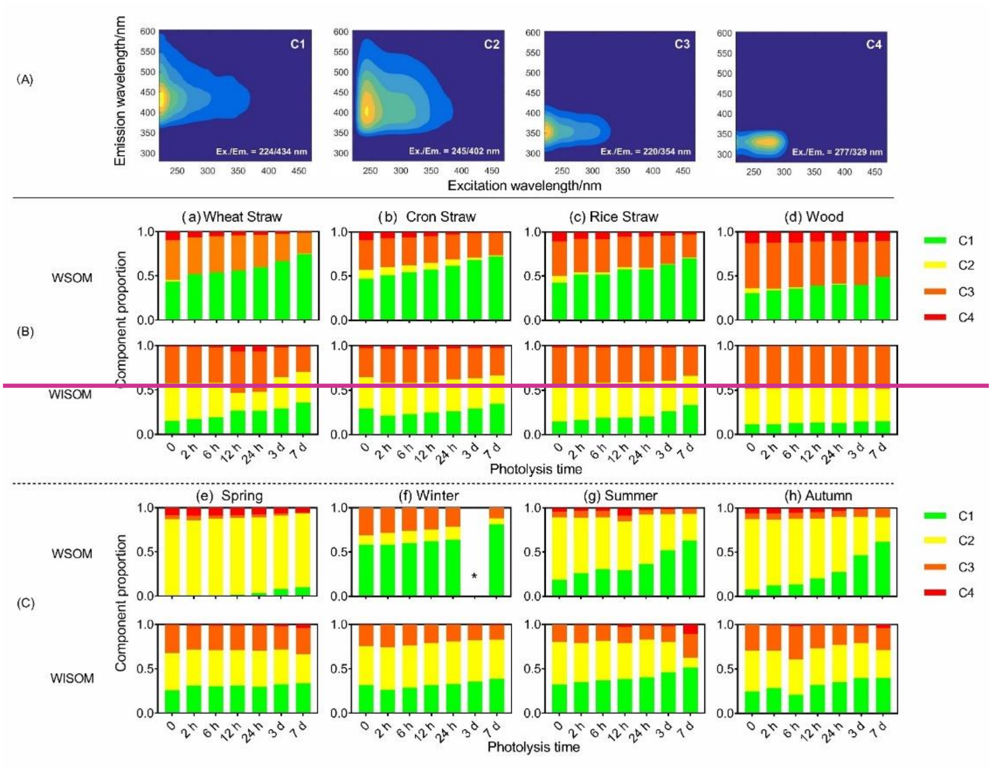
The attenuation rate constant of TFV in ambient PM (k = 0.04 h^{-1}) is lower than that in POA (k = 0.07 h^{-1}). In ambient PM, TFV of MSOM decreases by 79.4% but WSOM decreases by 26.7%

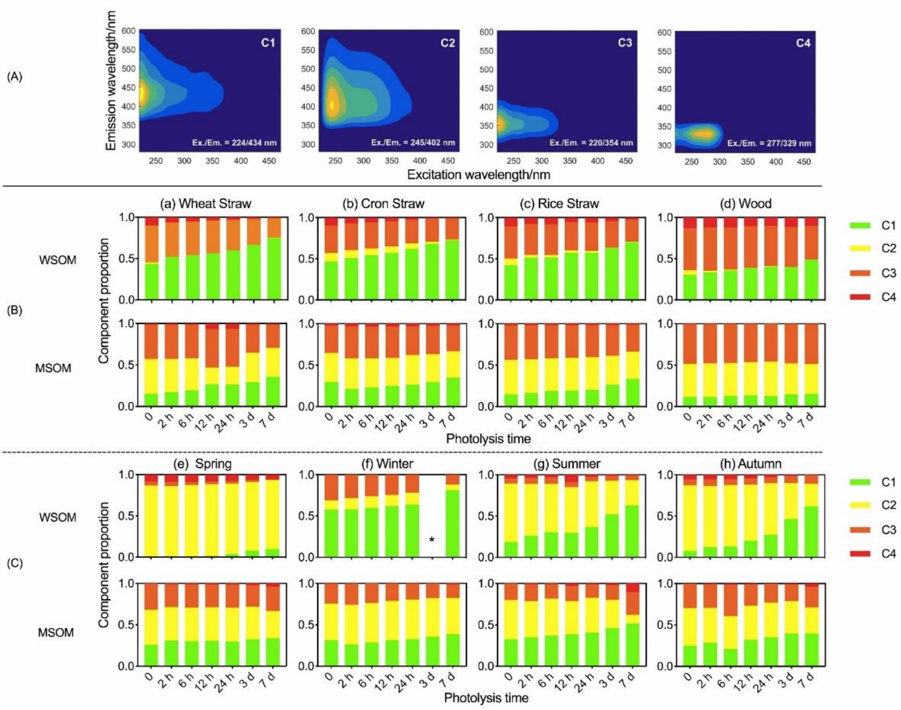
(**Figure 2(C)**). The attenuation of TFV and carbon content is identical with each other. The results suggest that MSOM has greater ability to be photodegraded than WSOM in ambient PM. It is worth noting that 72 h could be considered as the end point of aerosol photo-aging because TFV maintains a constant value after 72 h both in POA and ambient PM.

COM can be decomposed and transformed due to photodegradation in aerosol (Wong et al., 2015). Fluorophores ~~compositions~~ are studied by the approach of EEMs-PARAFAC~~ (**Fig.3A**).~~. Although previous study has analyzed the water-soluble and ~~water-insoluble~~methanol-soluble fluorophores separately (Tang et al., 2020a), based on the Chen's studies (2020; 2016b), water-soluble and ~~water-insoluble~~methanol-soluble samples were combined to create the PARAFAC model to illustrate the distribution of fluorophores in WSOM and ~~WISOM~~MSOM and solvent had no significant effect on the EEMs of complex mixtures in ~~aerosols. Four fluorophores are identified. Four~~aerosol. As shown in **Figure 3(A)**, four fluorophores are identified. The fluorescence peaks of C1 and C2 appear at (Ex./Em. = 224/434 nm) and (Ex./Em. = 245/402 nm). 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 are associated with protein-like organic matter (PLOM-1 and PLOM-2) (Sierra et al., 2005; Huguet et al., 2009; Chen et al., 2016a and 2016b; Coble, 2007; Fellman et al., 2009).

The content of fluorophores changes significantly during the photodegradation process. In POA (~~**Fig.3B**),~~**Figure 3(B)**), the relative content of high-oxidation HULIS (C1) increases ~~significantly in WSOM and the relative content increases~~ by ~~25.7% on average. Low oxidation HULIS (C2) and PLOM (C3&C4) decrease by 6~~63.0% and ~~19.7%, respectively.~~the relative content of low oxidation HULIS (C2) decreases by 88.0% in WSOM. Changes in proportion ~~indicates~~indicate that high-oxidation HULIS ~~fluorophores~~fluorophore (C1) could be generated and low oxidation HULIS~~(C2) and PLOM (C3&C4) may be photolyzed, which suggest that low oxidation HULIS~~ (C2) ~~could~~may be converted into high oxidation HULIS (C1) due to photooxidation (Tang et al., 2020b; Chen et al., 2020). ~~Furthermore,~~PLOM (C3&C4) decreases 19.7%, which indicates PLOM (C3&C4) can be photodegraded. In MSOM of POA, no regularity of variation is found in low oxidation HULIS (C2) and PLOM (C3&C4) and the content of high-oxidation HULIS (C1) ~~also~~ increases ~~(average~~by 17.5~~%) in WISOM,~~%, which can be attributed to photo-mediated secondary reaction.

~~In ambient PM (**Fig.3C**), the content~~The contents of PLOM (C3&C4) in ambient PM (~~43.3%)~~ ~~is~~ 19.4%) (**Figure 3(C)**) are significantly lower than that in POA (~~19.4~~43.3%). The content of high-oxidation HULIS ~~increases~~ (C1) multiplied 6.9 times and the low-oxidation HULIS (C2) decreases~~,~~ ~~which are~~ by 40.2% in WSOM, the variation is similar to POA. Thus, high-oxidation HULIS could be used to trace the degree of aerosols photo-aging. In MSOM of ambient PM, the content of high-oxidation HULIS (C1) increases by 43.5% and no regularity of variation is found in low oxidation HULIS (C2) and PLOM (C3&C4).



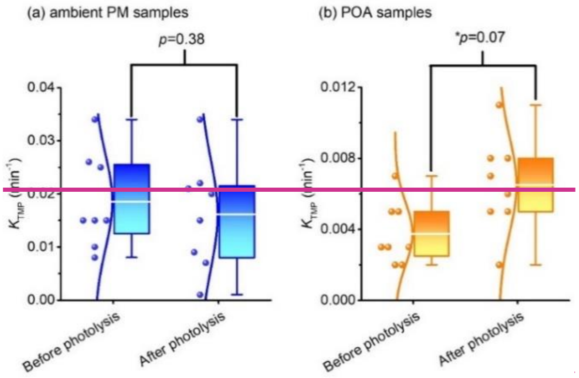


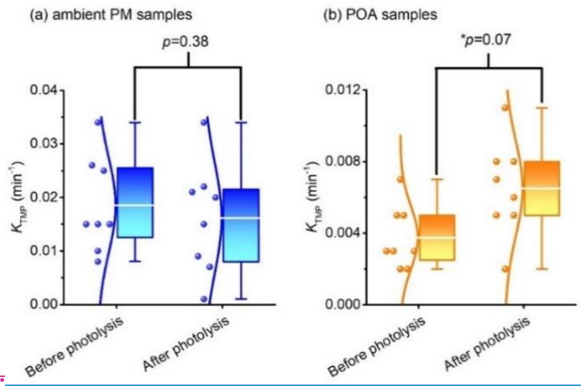
~~Fig.~~

Figure 3 (A) EEM spectra of fluorophores; (B) Changes in proportion of fluorophores in POA; (C) Changes in proportion of fluorophores in ambient PM. *: The data of 3-day photolysis of water-soluble ~~chromophores~~fluorophores in winter is unavailable.

3.3 Effect of COM photodegradation on aerosol photochemical reactivity

COM photodegradation has a significant effect on ~~aerosol~~ photochemical reactivity~~.~~ of COM in aerosol. The photochemical activity is ~~characterized~~quantitative analyzed by the yield of ^{3}COM* and $^1O_2$. ~~**Fig.4** show~~Only WSOM of original and photolyzed samples was used to measure the ~~difference~~yield of ^{3}COM* (Original samples with photodegradation time of 0, photolyzed samples with photodegradation time of 7d; details of samples are described in section 2.2). **Figure 4** shows the variation of triplet state generation before and after the photodegradation (~~Details~~Consumption curves of TMP are shown in **Figure S8**). In ambient PM, compared with original samples, the generation rate of triplet state decreases by 11% on average ~~after COM photodegradation~~in photolyzed samples, while statistical analysis shows that the changes ~~of triplet state generation~~ are not obvious ($p = 0.38$, two-tailed test). On the contrary, in POA, photodegradation ~~promote~~promotes triplet state generation significantly, the triplet state generation rate increases by 75% on average in ~~POA~~photolyzed samples. ($p = 0.07$, two-tailed test). ~~Triplet~~The results that triplet state generation remains unchanged or increases in different aerosols following photodegradation~~. The results~~ are unexpected and can be explained by recent study (Chen et al. 2021): ~~On~~on the one hand, only a small proportion of ~~COM~~water-soluble OM could generate triplet state in ~~aerosols~~aerosol and ~~Fluorophores does~~fluorophores do not represent the ~~COM~~OM with the ability to generate triplet state. Therefore, triplet state generation could not be evaluated only by fluorescence intensity. On the other hand, we use a high concentration of TMP, in this case, TMP mainly ~~capture~~captures high-energy triplet state (Rosado-Lausell et al., 2013; Chen et al., 2021). Thus, COM, that could generate a high-energy triplet state, may not be photodegraded in ambient PM.





~~Fig.~~

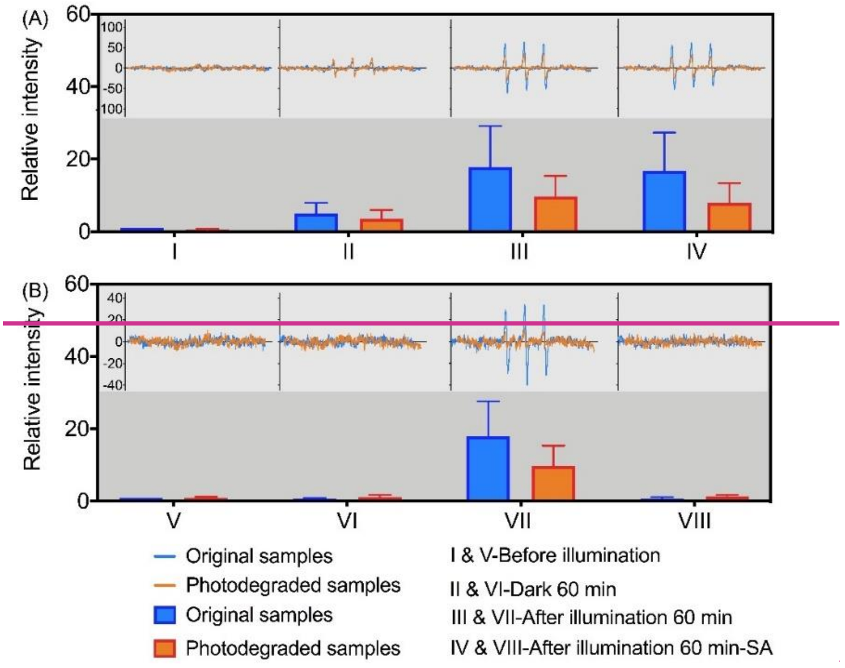
Figure 4 Changes in the triplet state generation. (a) Ambient PM; (b) POA. The line from bottom to top in the box plots are minimum, first quartile, the average value (white lines), third quartile, and maximum, respectively. The *p*-value is the probability that two sets of data have the same level (two-tailed test). * represents a significant difference at the 0.1 level.

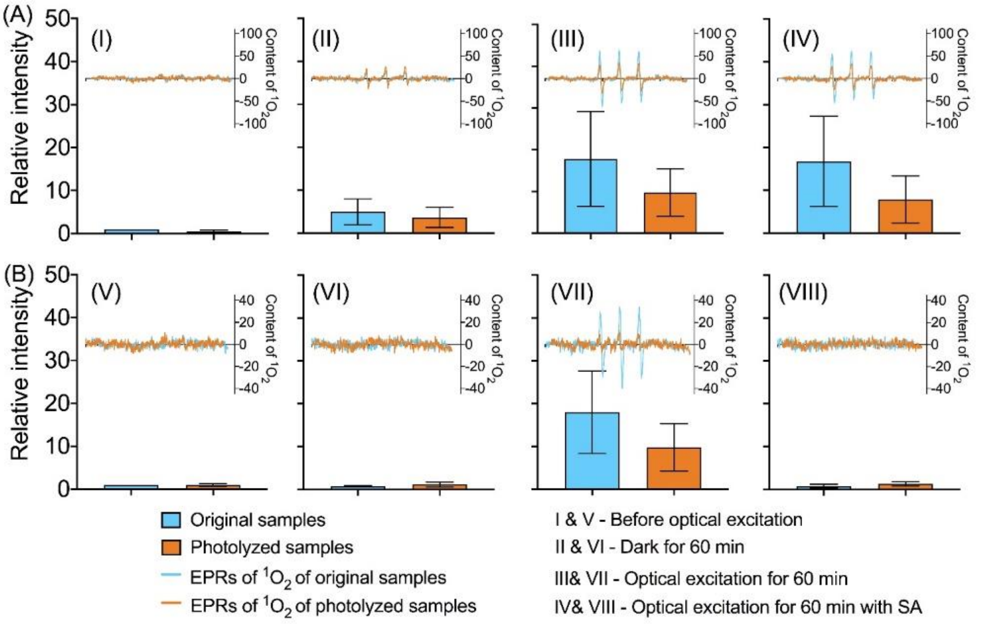
COM can generate triplet state and further generate singlet oxygen (McNeill and Canonica, 2016). The effect of COM photodegradation on singlet oxygen is studied. WSOM of original and photolyzed samples was used to measure the yield of $^1O_2$ (EPR spectra of all samples is shown in **Figure S9** and **Figure S10**). As shown in **Figure 5**, a decrease in the yield of $^1O_2$ reveals the inhibiting effect of COM photodegradation on photochemical activity both in ambient PM and POA. In POA, as shown in **Figure 5(A)**, (I) Before optical excitation, there is little $^1O_2$ both in original and photolyzed samples; (II) After 60 min in dark, $^1O_2$ are generated both in original and photolyzed samples, which suggests POA could generate $^1O_2$ without optical excitation. The content of $^1O_2$ in original samples is higher than that in photolyzed samples; (III) After 60 minutes of optical excitation, as expected, compared with the samples without optical excitation, the content of $^1O_2$ increases by 3 times both in original and photolyzed samples. The content of $^1O_2$ in original samples is also higher than that in photolyzed samples (42.1%), which prove the inhibiting effect of COM photodegradation on $^1O_2$ generation; (IV) However, the content of $^1O_2$ is nearly unchanged when the triplet state is quenched by sorbic acid. Therefore, the 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, because sorbic acid is a capturing agent for high-energy triplet state (triplet energies E_T = 239-247 kJ/mol) (Zhou et al., 2019; Moor et al., 2019). ~~Typical EPR spectra of $^1O_2$ are shown in **Fig.5** (EPR spectra of all samples are shown in **Figure S9** and **Figure S10**). In the original POA samples (i.e., the original samples with photodegradation time of 0, the photodegraded samples with photodegradation time of 7d; details of samples are described in section 2.2),~~In addition, COM photodegradation does not change the mechanism of low-energy ^{3}COM* generating $^1O_2$ in POA.

~~In POA, (I) there is little $^1O_2$ before illumination both in original and photodegraded samples; (II) $^1O_2$ 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, which suggest POA could generate $^1O_2$ without illumination; (III) As expected, compared with the samples without illumination, the content of $^1O_2$ increases by 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%), which prove the inhibiting effect 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. Sorbic acid is a capturing agent for high-energy triplet state (triplet energies E_T = 239-247 kJ/mol) (Zhou et al., 2019; Moor et al., 2019). Therefore, the 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.~~

In ambient PM, as shown in **Figure 5(B),** (V) Before optical excitation, the content of $^1O_2$ is very low in original and ~~photodegraded~~photolyzed samples, which is similar to POA; (VI) Compared with (V), the content of $^1O_2$ is almost unchanged after 60 min in dark, which is ~~opposite to~~different from POA. The result suggests ambient PM could not generate $^1O_2$ without ~~illumination.~~optical excitation. (VII) ~~The~~After 60 minutes of optical excitation, 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~~photolyzed samples (41.0~~%).~~% higher). (VIII) When the triplet state is quenched by sorbic acid, ~~the signal of~~ $^1O_2$ ~~disappears~~does not be generated. The result suggests that the precursor of $^1O_2$ is quenched and $^1O_2$ is mainly generated by high-energy ^{3}COM* in ambient PM. ~~The above results show that~~COM with the ~~precursor~~ability of generating high-energy triplet state could be photodegraded, which directly ~~lead~~leads to the decrease in $^1O_2$ in ambient PM. ~~In summary, a decrease in the yield of $^1O_2$ because the inhibiting effect of COM photodegradation on photochemical activity in ambient PM and POA and COM photodegradation do not change the mechanism of low-energy ^{3}COM* generating $^1O_2$ in POA. However, the~~ The quenching effects of sorbic acid on triplet state in POA and ambient PM are different because of the ~~difference in ^{3}COM*~~different energy of triplet state.





~~Fig.~~

Figure 5 Changes in ~~DOM~~COM generating $^1O_2$ before and after photodegradation. (A) POA; (B) Ambient POA.

4. Implication

We made a comprehensive study in COM ~~photo-degradation~~ photodegradation and the effect of COM ~~photo-degradation~~ photodegradation on optical ~~properties~~property, chemical ~~compositions~~component, and photochemical ~~activity. The~~ reactivity to reveal the characteristics of COM ~~photo-degradation were revealed.~~photodegradation. COM photodegradation could result in reduction of ~~carbonaceous components~~carbon content, attenuation of optical ~~properties~~property, and ~~changes~~change in ~~components.~~fluorescent component. We also ~~propose~~proposed that ~~the~~ COM photodegradation should be evaluated from ~~the~~ three aspects for further study. (1) The impact of COM photodegradation on ~~carbonaceous~~carbon content ~~are~~was 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~~suggested that changes in ~~carbonaceous component is~~carbon content were different in aerosols, which could be attributed to the differences in original components. (2) ~~Decreasing~~Attenuation in optical properties ~~is~~was significant. Absorption coefficient and fluorescence intensity ~~can~~could be thought of as a tracer for molecular weight (Stewart & Wetzel, 1980). Therefore, optical properties ~~could indicate~~indicated 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) COM Photodegradation ~~of COM~~ may ~~dominant~~dominate the fluorophores components (Aiona et al., 2018; Timko et al., 2015). High~~-~~ molecular~~-~~ weight COM could be decomposed into low~~-~~ molecular~~-~~ weight COM during the photodegradation process. The conversion of low-oxidation HULIS to high-oxidation HULIS ~~is~~was observed. Changes in COM may represent the oxidation degree of organic substances~~ oxidation~~.

Therefore, we suggested that optical parameter and ~~degree of~~ oxidation degree of organic molecules should be use for characterizing the aerosol photo-aging process (Maizel et al., 2017).

Photodegradation ~~can~~could not only change the properties and components of COM, but also change their photochemical ~~activity~~reactivity, which ~~furtherly has~~further had 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). Photochemical ~~activity~~reactivity was quantified by the yield of triplet state and $^1O_2$~~.~~ in our study. However, two different methods, two different results. COM photodegradation ~~can~~could restrain $^1O_2$ generation but the effect of photodegradation on ^{3}COM* ~~are~~was unclear. Photodegradation ~~has~~had a significant inhibiting effect on the $^1O_2$ yield in aerosols (Latch et al. 2006; Chen et al., 2018). We ~~insist~~insisted that aerosol aging would be changed by photodegradation due to the yield of $^1O_2$ ~~is~~was changed. Changes in triplet state generation ~~are~~were uncertain in ambient PM and POA. There ~~are~~were two reasons for ~~it~~this. On the one hand, only a small amount of COM ~~are~~was the precursor of ^{3}COM* in aerosols. On the other hand, the energy of capturing agents was closely related to ^{3}COM* quantification and thereby ^{3}COM* could not be captured completely. Other capturing agents may lead to different results. Thus, ^{3}COM* could not properly illustrate ~~photo-degradation.~~photodegradation. COM photodegradation ~~would be~~could play an important role in the content of ROS and ROS could ~~celebrate~~calibrate the COM photooxidation (Claeys et al., 2004). Given the results, the interaction effect ~~is~~was significant in aerosol.

In summary, atmospheric photochemistry process ~~has~~had a remarkable impact on aerosol aging. Prediction of atmospheric lifetime and improvement of quality ~~are~~were strongly associated with photochemistry. We ~~prove~~proved that ~~carbonaceous~~carbon content, absorption ~~coefficients~~coefficient, fluorescence intensity, and photochemical ~~activities are~~reactivity were useful to reflect COM photodegradation process and aerosol fate. In addition, COM photodegradation ~~have~~had a different impact on chemical ~~activity~~reactivity in different aerosols, which may have different mechanisms. Therefore, the mechanisms of COM photodegradation ~~effecting~~affecting aerosol photo-aging ~~deserve~~deserved 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−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.

Acknowledgments. We thank the National Natural Resources Foundation for its financial support.

Financial support. This work was supported by the National Natural Science Foundation of China (grant numbers 41877354 and 41703102), and the Youth Science and Technology Nova Program of Shaanxi Province (2021KJXX-36).

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