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 photosensitivity, thus COM has a potential contribution to aerosols aging. However, the effect of COM photodegradation on photochemical reactivity and aerosol aging are not fully understood. Here, we report the potential impacts of photodegradation on carbonaceous components, optical properties, fluorophores components, and photochemical reactivity. We confirm that both water-soluble and water-insoluble COM are photodegraded, and fluorescent intensities decrease by 70% on average. Furthermore, low oxidation humic-like substance (HULIS) is converted into high oxidation HULIS, the result suggests that oxidation of HULIS can be used to trace the degree of aerosols aging. COM Photodegradation has a significant impact on photochemical reactivity. The content of triplet state COM decreases slightly in ambient particulate matter but increases in primary organic aerosol following photodegradation. The result highlight that photodegradation has opposite effect on different aerosols as a result of the changes in components. The ability of COM generating singlet oxygen declines obviously, which is consistent with optical properties. Photodegradation of precursors limit singlet oxygen generation and affect the aerosol photochemistry process. In conclusion, COM photodegradation not only change the compositions and properties, but also change aerosol aging.

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

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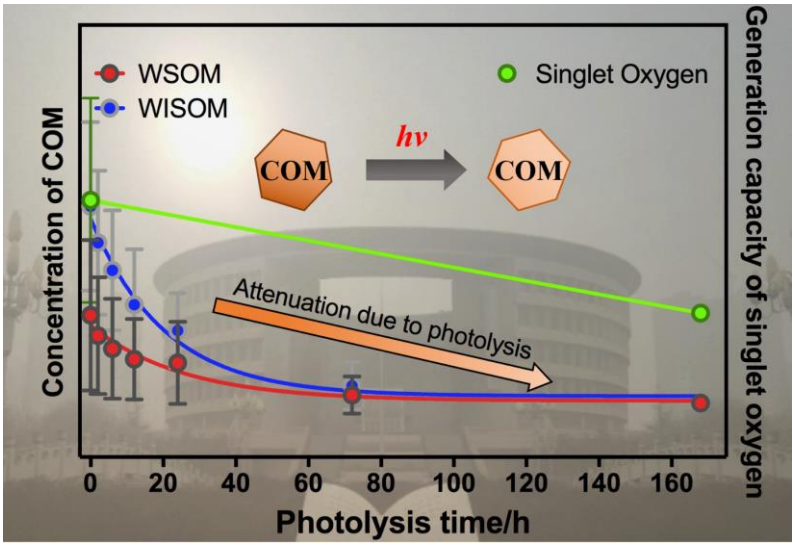

1. Introduction

Atmospheric chromophoric organic matter (COM) mainly originate from biomass combustion emissions and secondary aerosols (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 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 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 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. On the other hand, photodegradation has a significant effect on the composition of COM. Photodegradation can cause that COM decompose into small molecules and COM may have lower volatility and higher oxidation degree after photodegradation (Grieshop et al., 2009). COM could also be generated, 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. 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 photochemical activity in turn. There are limited studies that comprehensive exploring the components and properties transformation of COM in aerosols during the photodegradation processes.

Atmospheric COM could participate in the complex photochemical reaction, which further affect the aerosol aging (Mang et al., 2008). On the one hand, COM participates in atmospheric photochemical processes as a reactant. 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). 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 participates in atmospheric

photochemistry process indirectly through generating reactive intermediates. 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 ($\bullet O_2^-$) 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 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 of ^{3}COM*. Probes, such as 2,4,6-trimethylphenol (TMP) and sorbic acid (SA), are applicable to evaluate 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 is necessary to clarify the path and mechanism.

COM photochemistry may dominate the chemical composition and aerosol aging. 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 laboratory. The objectives of the study are (1) to clarify the characteristics of carbonaceous components variation during COM photodegradation process, (2) to explore the effects of photo-degradation on the fluorophores and optical properties of water-soluble and water-insoluble chromophores, and (3) to investigate the effects of COM photodegradation on photochemical reactivity and aerosol aging (photochemical reactivity is characterized by 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 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 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 of combustion

equipment 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 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 times were 0 h, 2 h, 6 h, 12 h, 24 h, 3 d and 7 d, respectively. Two capsules (**Figure S2(b) & (c)**) were designed for triplet state and ROS generation experiment.

2.3 Carbonaceous components analysis

The original and photolyzed 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 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). The blank samples were also extracted with the same method.

The analytical method of carbonaceous components has been described previously (Mu et al., 2019). Briefly, 100 μL extracts were injected on the baked quartz filter. Then, the wet filters were dried out by a rotary evaporator and the dried filters 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).

2.4 Optical analysis

The light absorption and EEM spectra of the extracts were measured by an Aqualog fluorescence spectrophotometer (Horiba Scientific, America). 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)). WSOM and WISOM (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 of the models are shown in **Figure S4** of SI).

2.5 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 ^{3}COM* generation

ability before and after 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 (**Figure S2(b)**). The capsule was placed in the reactor (**Figure S2(a)**). 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 at different time points 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). The 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 & Anastasio (2018) and Richards-Henderson et al. (2015) have reported that TMP consumption conform to first-order kinetics. 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}):

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

2.6 Singlet oxygen generation experiment

The effects of the COM 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 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 (**Figure S2(c)**). Then, 50 μL of the mixed solution was taken out by capillary for EPR analysis; (2) 40 μL WSOM, 40 μL TEMP and 40 μL ultra-pure water were mixed. 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) 40 μL WSOM, 40 μL TEMP and 40 μL ultra-pure water were mixed. The capsule was illuminated in the reactor for 60 min. 50 μL mixed solution was taken out by capillary for EPR analysis; (4) 40 μL WSOM, 40 μL TEMP and 40 μL SA solution were mixed. The capsule 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

COM can be decomposed and transformed in aerosol due to photodegradation (Wong et al., 2015). **Fig.1** describes the changes in the content of carbonaceous components before and after COM photodegradation. In POA, water soluble and water insoluble organic carbon (WSOC and WISOC) 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)**, 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. 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. The proportions of OC1, OC2-4, and OPC are relatively stable in ambient PM, which indicate that the decreasing proportion in the different stage are similar and the tendency is also opposite to POA. The result reflects that 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.

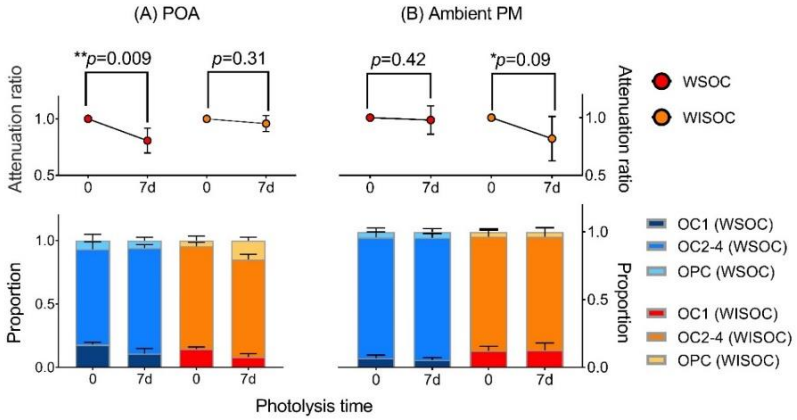

Fig.1 Changes in carbonaceous components before and after photodegradation. The *p*-value is the probability that two sets of data have the same level (two-tailed test). * and ** are represent the significant difference at the 0.1 and 0.01 levels, respectively.

3.2 Effect of COM photodegradation on optical properties

As shown in **Fig.2**, both absorption coefficients and total fluorescence volume (TFV, RU-nm^2/m^3) significantly decrease following aerosol photodegradation, which suggest that COM are photo-bleached (Aiona et al., 2018; Duarte et al., 2005; Liu et al., 2016). The attenuations of fluorescence and absorption coefficients are fit to first-order decay. The absorption coefficients decrease by 32.0% and TFV decreases by 71.4% on average. 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.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 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.

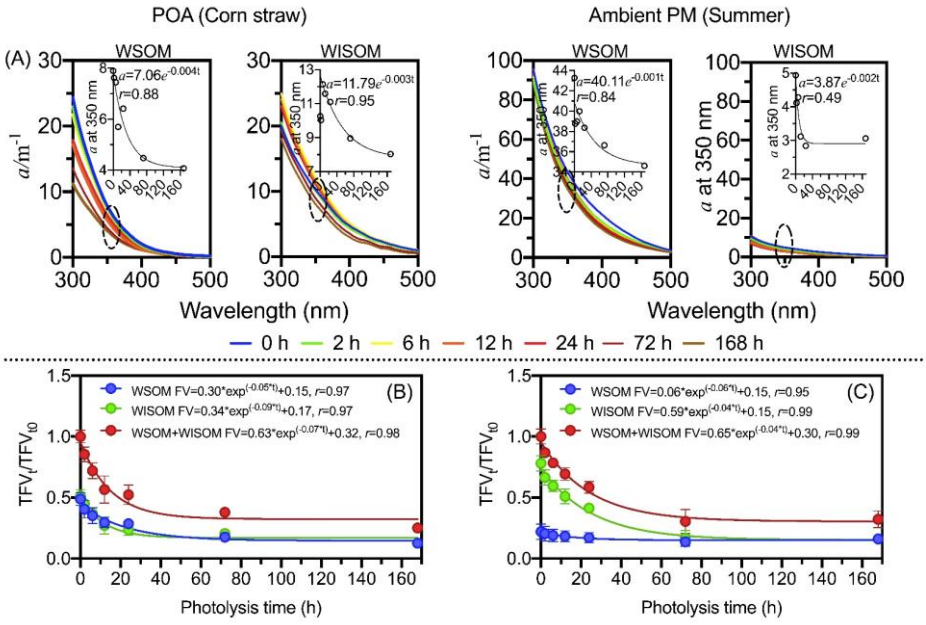

Fig.2 Changes in light absorption and fluorescence volume during the photodegradation process. (A) Absorption coefficient. The scatter plot is absorption coefficient at 350 nm. (B) and (C) the attenuation curve of fluorescence volume in POA (except for the wood sample) and ambient PM, respectively.

Fluorophores compositions are studied by the approach of EEMs-PARAFAC (**Fig.3A**). Although previous study analyzed the water-soluble and water-insoluble fluorophores separately (Tang et al., 2020a), based on the Chen's studies (2020; 2016b), water-soluble and water-insoluble samples were combined to create the PARAFAC model to illustrate the distribution of fluorophores 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). 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**), the 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 6.0% and 19.7%, respectively. Changes in proportion indicates that high-oxidation HULIS fluorophores (C1) could be generated and low oxidation HULIS(C2) and PLOM (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). Furthermore, the content of high-oxidation HULIS (C1) also increases (average 17.5%) in WISOM, which can be attributed to photo-mediated secondary reaction.

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 content of high-oxidation HULIS increases and the low-oxidation HULIS decreases, which are similar to POA. Thus, high-oxidation HULIS could be used to trace the degree of aerosols aging.

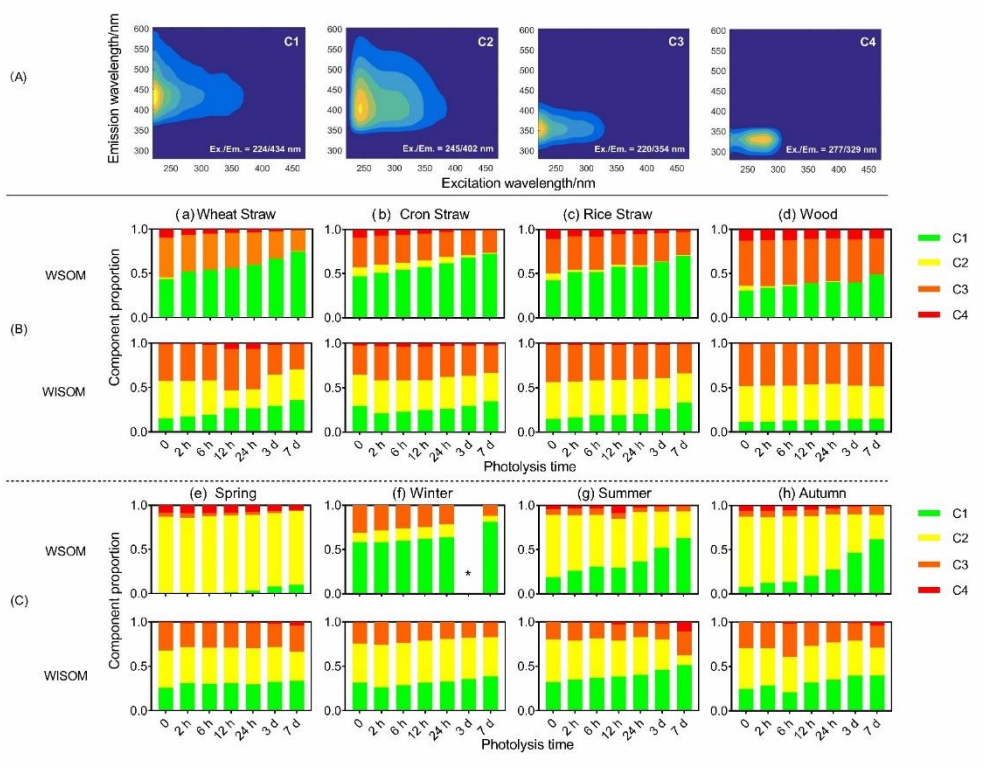

Fig.3 (A) EEM spectra of fluorophores; (B) Changes in proportion of fluorophores in POA; (C) Changes in proportion of fluorophores in ambient PM. *: The data of 3-day photolysis of water-soluble chromophores in winter is unavailable.

3.3 Effect of COM photodegradation on aerosol photochemical reactivity

COM photodegradation has a significant effect on aerosol photochemical reactivity. The photochemical activity is characterized by the yield of ^{3}COM* and $^{1}O_2$. **Fig.4** show the difference of triplet state generation before and after the photodegradation (Details are shown in **Figure S8**). In ambient PM, the generation rate of triplet state decreases by 11% on average after COM photodegradation, while statistical analysis shows that the changes of triplet state generation are not obvious (p = 0.38, two-tailed test). On the contrary, photodegradation promote triplet state generation significantly, the triplet state generation rate increases by 75% on average in POA (p = 0.07, two-tailed test). Triplet state generation remains unchanged or increases following photodegradation. The results are unexpected and can be explained by recent study (Chen et al. 2021): On the one hand, only a small proportion of COM could generate triplet state in aerosols and Fluorophores does not represent the COM with the ability to generate triplet state. Therefore, triplet state generation could not be evaluated by fluorescence intensity. On the other hand, we use a high concentration of TMP, in this case, TMP mainly capture 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.

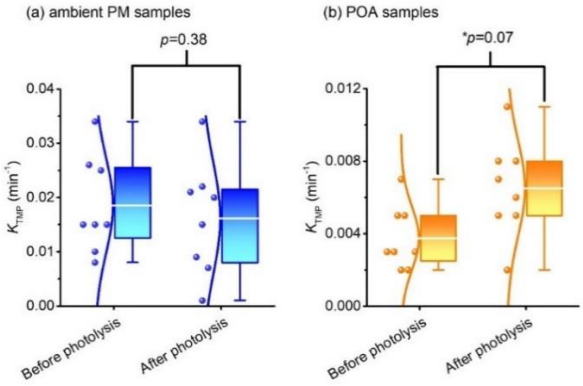

Fig.4 Changes in the triplet state generation. (a) Ambient PM; (b) POA. The line from bottom to top in the box plots are minimum, first quartile, the average value (white lines), third quartile, and maximum, respectively. The *p*-value is the probability that two sets of data have the same level (two-tailed 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. 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 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, (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 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 quenching effects of sorbic acid in POA and ambient PM are different because of the difference in ^{3}COM* energy.

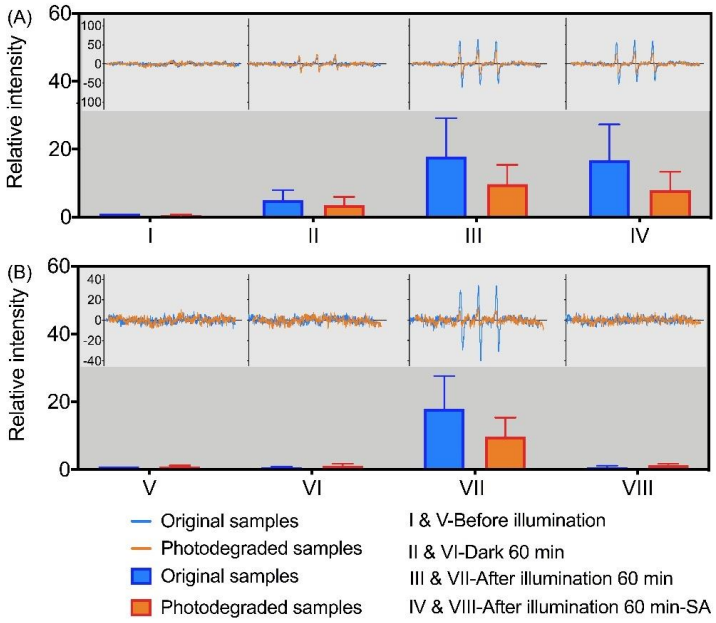

Fig.5 Changes in DOM generating $^1O_2$ before and after photodegradation. (A) POA; (B) Ambient POA.

4. Implication

We made a comprehensive study in COM photo-degradation and the effect of COM photo-degradation on optical properties, chemical compositions, and photochemical activity. The characteristics of COM photo-degradation were revealed. COM photodegradation could result in reduction of carbonaceous components, attenuation of optical properties, and changes in components. 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. (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) Photodegradation of COM may dominant the fluorophores components (Aiona et al., 2018; Timko et al., 2015). High-molecular-weight COM could be decomposed into low-molecular-weight COM during photodegradation process. The conversion of low-oxidation HULIS to high-oxidation HULIS is observed. Changes in COM may represent 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).

Photodegradation can not only change the 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). Photochemical activity was quantified by the yield of triplet state and $^1O_2$. 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. On the one hand, only a small amount of COM are the precursor of ^{3}COM* in aerosols. 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. Thus, ^{3}COM* could not properly illustrate photo-degradation. 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.

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 carbonaceous content, absorption coefficients, fluorescence intensity, and photochemical activities are 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, the mechanisms of COM photodegradation effecting 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−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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