

1 **Aqueous OH-initiated photooxidation of smoke extracts from maize**
2 **straw and coal combustion: optical character and molecular**
3 **composition**

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10 **Abstract:** Aqueous-phase •OH photodegradation of coal- and maize-derived smoke

11 extracts was investigated to elucidate their optical and molecular transformations.

12 Parallel factor analysis of excitation-emission matrix fluorescence spectra identified

13 one humic-like and two protein-like substances. FT-ICR MS revealed that CHO

14 (74.5% for maize, 58.9% for coal) and CHON (24.1% for maize, 11.8% for coal)

15 compounds dominated both smoke extracts, whereas sulfur-containing species were

16 more abundant in coal smoke (29.4%) than in maize (1.4%). The aqueous •OH

17 photooxidation enhanced molecular saturation and reduced aromaticity, reflected by

18 lower double bond equivalent and aromaticity index values. The abundance of

19 lignin-like compounds decreased, whereas lipid- and aliphatic-like fractions increased,

20 suggesting a transformation of aromatic species into more saturated products, which

21 correspondingly reduced light absorption and overall fluorescence intensity. Distinct

22 photodegradation pathways were observed for coal and maize extracts based on

23 changes in resistant, degraded, and newly formed molecules. Reactive species

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24 contributed to WSOC degradation in the order $\bullet\text{OH} > {}^3\text{C} > {}^1\text{O}_2$, with contributions of
25 86.4%, 12.8%, and 0.8% for coal extracts, and 80.9%, 16.0%, and 3.1% for maize
26 extracts, respectively. Increased oxalic acids, CHO_2^+ fragments, and declining pH
27 values during the first 5 h indicated substantial formation of carboxylic acids.
28 Measurements from aerosol mass spectrometry showed increasing oxidation
29 indicators during this early stage, confirming enhanced oxidation of aqueous
30 secondary organic aerosol. Oxidative potential, assessed by dithiothreitol
31 consumption, initially increased and then declined, while its normalization by
32 water-soluble organic carbon increased, likely due to the formation of
33 nitrogen-containing compounds in coal smoke and reactive quinones in maize smoke,
34 respectively. Overall, this study improves understanding of aqueous-phase
35 photochemical processing of smoke-derived water-soluble organic matter and
36 supports more accurate representation of these processes in atmospheric models,
37 contributing to better assessments of smoke aging impacts on air quality and climate.

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in light absorption and total fluorescence intensity.

38 **Keywords:** molecular transformations, optical characteristic, FT-ICR MS, reactive
39 species, dithiothreitol (DTT) consumption rate

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41 **1 Introduction**

42 The atmospheric aqueous phase contains a variety of oxidants, such as hydrogen
43 radical ($\bullet\text{OH}$), peroxy radicals, singlet oxygen (${}^1\text{O}_2$), and excited triplet states of
44 organic compounds (${}^3\text{C}^*$), which can trigger aqueous-phase oxidation reaction.
45 Aqueous-phase process has been recognized as a significant source of secondary
46 organic aerosol (SOA) and key contributors to light-absorbing compounds, thereby

47 influencing radiative forcing and air quality (Arciva et al., 2024; Go et al., 2023).
48 Extensive studies have investigated the chemical composition, light-absorption
49 properties, and SOA mass yield from single-component model compounds (Arciva et
50 al., 2022; Li et al., 2022). Recently, increasing attention has been toward the aqueous
51 photoaging of complex mixtures, including laboratory-generated SOA or
52 multicomponent systems (Gerritz et al., 2024; Go et al., 2024). Moreover, studies on
53 aqueous aging of water-soluble organic matter (WSOM) derived from actual smoke
54 particle or PM_{2.5} extracts provide valuable insights into aqueous-phase processing
55 under more realistic atmospheric conditions (Fan et al., 2018; Hems et al., 2020;
56 Wong et al., 2017). Organic matter (OM) within smoke particles, which accounts for
57 up to 60-90% of total mass, is a complex mixture of aromatic and aliphatic
58 compounds with diverse functional groups. The chemical complexity of these
59 precursors poses challenges for comprehensive product characterization and
60 mechanistic studies. Molecular-level compositional data are therefore crucial for
61 improving our understanding of the role of smoke-derived OM in atmospheric
62 aqueous-phase chemistry. High-resolution mass spectrometry (MS) techniques with
63 soft ionization methods, such as Fourier transform ion cyclotron resonance mass
64 spectrometry (FT-ICR MS), enable detailed molecular characterization in complex
65 mixtures and have been widely applied in aerosol studies (Cao et al., 2025; Wang et
66 al., 2017).

67 To date, only a few studies (Leresche et al., 2021; Lei et al., 2024) have
68 examined photochemical aging characteristics of aqueous extracts of smoke particles
69 or atmospheric fine particulate matter, most of which have appeared only recently.
70 Notably, few investigations have compared the molecular and optical changes during
71 aqueous-phase oxidation of smoke extracts from different fuel sources. Cao et al.

72 (2025) compared molecular-level composition and fluorophore changes of extracted
73 WSOM, but their study did not consider the distinct contributions of various reactive
74 oxygen species (ROS) to the oxidation process. Additionally, the wavelength of the
75 light source can significantly influence the photochemical reactivity of organic
76 compounds. For instance, syringaldehyde was found to inhibit the degradation of
77 vanillyl alcohol under UV-B irradiation due to light-absorbing competition, whereas it
78 promoted the degradation of vanillyl alcohol under UV-A irradiation via the
79 photosensitization effect of syringaldehyde (Li et al., 2024).

80 To elucidate the reaction mechanism involved in aqueous-phase photooxidation,
81 it is crucial to understand the formation, transformation, and roles of ROS during
82 photolysis. Biomass burning smoke—such as that produced from agricultural crop
83 residues—contains a variety of potential organic photosensitizers bearing with
84 carbonyl groups and conjugated double bonds, which can absorb sunlight and
85 generate ROS (e.g., HO_2/O_2^- , $^1\text{O}_2$, αOH), thereby enhancing atmospheric oxidative
86 capacity. However, direct quantification of ROS remains challenging (Gerritz et al.,
87 2024; Leresche et al., 2021; Manfrin et al., 2019). For instance, Gerritz et al. (2024)
88 investigated the photolytic formation of ROS in aqueous extracts of
89 laboratory-generated SOA using an in situ UV-vis irradiation system coupled with
90 electron paramagnetic resonance (EPR) spectroscopy and identified organic peroxides
91 and carbonyls as major ROS precursors. Manfrin et al. (2019) reported the $^1\text{O}_2$
92 formation from photosensitized reactions mediated by aromatic SOA, although free
93 radicals were not directly measured. Due to the chemical complexity of
94 smoke-derived WSOM and the analytical difficulty in quantifying ROS, the
95 underlying reaction mechanisms remain poorly understood.

96 Further investigation into the aqueous photoaging of WSOM from different

97 combustion sources is crucial to understanding the underlying mechanisms driving
98 chemical transformation and light absorption. Comparative studies of maize- and
99 coal-derived WSOM under simulated sunlight can reveal how source-dependent
100 compositions influence photo-reactivity and light-absorbing compounds formation.
101 This study compares the optical, molecular evolution and oxidative potential of maize
102 (a representative agricultural residue) and coal smoke extracts during OH-induced
103 photooxidation. WSOM from both smoke types were analyzed using UV-vis
104 spectrometer, excitation-emission matrix (EEM) fluorescence, and FT-ICR MS to
105 identify similarities and differences in photoaging behavior. High-resolution
106 time-of-flight aerosol mass spectrometers (HR-AMS) were used to characterize the
107 bulk chemical composition of low-volatility organics (denoted as aqSOA) over
108 photoreaction. Our findings will provide insights into the chemical evolution and
109 environmental impacts of smoke-derived organic matter.

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111 **2 Materials and Methods**

112 **2.1 Chemicals and solutions**

113 The following reagents were purchased from the Sigma-Aldrich
114 (dithiothreitol, >99%; 5,5'-dithiobis (2-nitrobenzoic acid), >99%; benzoic acid, >99%;
115 syringol, >99%; furfuryl alcohol, >99%). Methanol ($\geq 99\%$), acetonitrile ($\geq 99\%$),
116 Na_2CO_3 ($\geq 99\%$) and NaHCO_3 ($\geq 99\%$) were purchased from Acros Chemicals.
117 Sulfuric acid ($\geq 99\%$) was obtained from Sinopharm. $(\text{NH}_4)_2\text{SO}_4$ (GR), H_2O_2
118 (29%~32%) and KOH($\geq 99\%$) were supplied by Aladdin and Alfa Aesar, respectively.
119 2,2,6,6-Tetramethylpiperidine ($\geq 98\%$) and 5,5-dimethyl-1-pyrroline N-oxide ($\geq 97\%$)

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120 were purchased from Anpel Laboratory Technologies (Shanghai) Co., Ltd.

121 All chemicals were used as received without further purification. All solutions
122 were prepared with ultrapure water (resistivity \geq 18.2 M Ω cm) produced by a Milli-Q
123 purification system.

124 2.2 Sample collection and experiment preparation

125 Coal and maize straw were collected from Lingwu (Ningxia) and Shangqiu
126 (Henan Province), respectively, and combusted in a self-built stove, designed to
127 simulate domestic fuel burning conditions. Smoke particle collection followed the
128 procedures described in our previous study (Ye et al., 2025). Briefly, the stove was
129 connected to a stainless steel dilution tunnel and residence chamber. Smoke particles
130 emitted from maize straw and coal combustion were collected on pre-baked quartz
131 fiber filters (20.3 \times 25.4 cm, Whatman) using two samplers equipped with cyclone
132 with a 2.5 μ m aerodynamic cutoff.

133 One quarter of each filter was cut into strips and placed in extraction bottles. The
134 samples were ultrasonically extracted three times with 30 mL Milli-Q water. The
135 combined extracts were filtered through a 0.45 μ m PTFE membrane and subsequently
136 diluted to approximately 15 mgC/L for photoaging experiment based on suggested
137 TOC level (0.5-1.4 mmol C/L) by Cook et al. (2017) for cloud water. Photochemical
138 reactions were performed in a Rayonet RPR-200 photoreactor equipped with 14
139 lamps, following the procedure described in our previous study (Ye et al., 2025). The
140 irradiance intensity on the solution surface was 2.4 mW/cm² in the wavelength region
141 of 290-400 nm (centered at 313 nm), as measured by a radiometer (Photoelectric
142 Instrument Factory of Everfine Corporation, Hangzhou, China). The intensity is slight

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143 lower than natural sunlight levels (6.16 mW/cm²) measured at noon during winter at
144 Jiangsu University of Technology (Wang et al., 2025). Before photooxidation, 10 mM
145 H₂O₂ was added to the reaction solution to generate $\cdot\text{OH}$ with certain concentration,
146 consistent with previous study (Arciva et al., 2022; Cao et al., 2025).

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147 2.3 Chemical analysis

148 Water-soluble organic carbon (WSOC) concentrations were determined using a
149 total organic carbon (TOC) analyzer (TOC-L CPH, Shimadzu, Japan). Metal element
150 concentrations (Fe and Cu) were quantified by inductively coupled plasma-mass
151 spectrometry (ICP-MS, Agilent 7800). Eight water soluble inorganic ions (Na⁺, Cl⁻,
152 SO₄²⁻, NO₃⁻, K⁺, NH₄⁺, Ca²⁺ and Mg²⁺) were also detected for both smoke extracts.

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153 Details can be found in Sect. S1 in the Supplement. These detection limits were
154 determined based on three times the standard deviation of blank sample. The method
155 detection limits ranged from 5-20 $\mu\text{g/L}$ for anions and 0.5-2 $\mu\text{g/L}$ for cations. The
156 detection limits of Fe and Cu are 2.0 $\mu\text{g/L}$ and 0.8 $\mu\text{g/L}$, respectively.

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157 2.4 UV-vis and EEM analysis

158 The UV-vis absorption spectra were monitored using UV-vis spectrophotometer
159 (Shimadzu, Japan) over wavelength range of 200-700 nm. The mass absorption
160 coefficients (MACs, m²/gC), defined as absorbance normalized by WSOC
161 concentration, were calculated as follows:

$$162 \quad \text{MAC}_\lambda = \frac{A_\lambda}{C \times L} \times \ln 10$$

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163 Where A_λ represent the absorbance at wavelength λ . C refers to the WSOC
164 concentration of reaction solution. L is the optical path length (1 cm in this study).

$$\text{MAC}_\lambda = \frac{A_\lambda}{C \times L} \times \ln 10$$

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165 The EEM spectra were recorded using a three-dimensional fluorescence

166 spectrophotometer (FluoroMax Plus, HORIBA Scientific). Parallel factor analysis
167 (PARAFAC) model was applied to EEM spectra to resolve the fluorescent compounds
168 using the DOMFluor toolbox in MATLAB 2021b. Details of the determination and
169 modeling procedures are provided in our previous study (Ye et al., 2025). Three
170 fluorescence components (C1, C2 and C3) were identified from PARAFAC model.
171 The fluorescence index (FI), humification index (HIX), and biological index (BIX)
172 were further calculated to characterize the fluorescent properties of the samples. The
173 calculation methods for these indicators were shown in the supplement and in our
174 previous study (Ye et al., 2025).

175 **2.5 FT-ICR MS measurement**

176 The molecular compositions, degree of unsaturation, and aromaticity of WSOM
177 were characterized using FT-ICR MS coupled with negative electrospray ionization
178 (ESI⁻). Solid-phase extraction (SPE) was employed for sample pretreatment prior to
179 FT-ICR MS determination, following procedures similar to those described in
180 previous studies (Yang et al., 2025). Briefly, the reaction solution was adjusted to pH
181 2 and pass through SPE cartridges (Oasis HLB, Waters, USA) preconditioned with 15
182 mL methanol and 10 mL Milli-Q water. The retained organic matter was subsequently
183 eluted with 10 mL methanol. The eluate was then concentrated to approximately 0.5
184 mL using a rotary evaporator and stored at -20 °C until analysis. Prior to analysis, the
185 sample was re-dissolved in 4 mL of methanol and filtered through a 0.22 μm PTFE
186 membrane. FR-ICR MS analysis was performed with a capillary voltage of 4.0 kV,
187 and samples were introduced into the ESI source at a flow rate of 120 μL/ h. Mass
188 spectra were acquired over the m/z range of 150 – 800 Da. To improve the
189 signal-to-noise ratio and dynamic range, each spectrum was averaged from 200 scans.

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190 Blank samples were analyzed under the same procedure. Notably, no water-insoluble
 191 precipitates larger than 0.22 μm were observed during photooxidation. However,
 192 filtration of the reaction solution through a 0.22 μm membrane prior to analysis may
 193 resulted in the loss of some newly formed oligomers.

194 The Composer software (Sierra Analytics, USA) was utilized to process the
 195 FT-ICR MS spectra and assign elemental compositions to recalibrated peaks, with a
 196 mass tolerance of ± 1.0 ppm and a signal-to-noise ratio (S/N) threshold of ≥ 4. Based
 197 on the assigned molecular formulas, WSOM compounds were categorized into four
 198 groups: CHO, CHON, CHOS, and CHONS. To evaluate the degree of unsaturation
 199 and aromaticity, double bond equivalent (DBE) and aromaticity index (AI) were
 200 calculated as follows:

$$201 \quad \text{DBE} = \frac{1}{2} \times (2c + 2 - h + n) \quad (2)$$

$$202 \quad \text{AI} = \frac{1 + c - 0.5o - s - 0.5h}{c - 0.5o - s - n} \quad (3)$$

203 The intensity-weighted averaged characteristic parameters can be expressed as:

$$204 \quad P_w = (\sum P_i I_i) / \sum I_i \quad (4)$$

205 where P represents DBE, AI, molecular weight (MW), oxygen-to-carbon (O/C) or
 206 hydrogen-to-carbon (H/C) ratio. P_i represents the corresponding parameter value for
 207 each individual compound I_i , and I_i represents the relative abundance of its molecular
 208 formula.

209 Molecular formulas were further classified into seven compound classes based
 210 on their H/C and O/C ratios (Ning et al., 2025): lipid-like ($1.5 < \text{H/C} \leq 2.0$, $0 \leq \text{O/C} \leq 0.3$);
 211 aliphatic -like ($1.5 < \text{H/C} \leq 2.2$, $0.3 < \text{O/C} \leq 0.67$); lignin-like ($0.67 < \text{H/C} \leq 1.5$, $0.1 \leq$

212 O/C < 0.67); carbohydrate-like ($1.5 < H/C \leq 2.5$, $0.67 < O/C < 1.2$); unsaturated
213 hydrocarbon-like ($0.67 < H/C \leq 1.5$, $O/C < 0.1$); unsaturated aromatic-like ($0.2 \leq H/C$
214 ≤ 0.67 , $O/C < 0.67$), and tannin- ($0.6 < H/C \leq 1.5$, $0.67 \leq O/C \leq 1.2$). The saturated
215 compounds were defined as the sum of lipid-like and aliphatic components.

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216 2.6 High-resolution mass spectrometry analysis

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217 High-resolution aerosol mass spectrometer (HR-AMS, Aerodyne Res. Inc.) was
218 used to characterize the bulk chemical composition of aqSOA, including average
219 elemental ratios (i.e., oxygen-to-carbon ratio (O/C) and hydrogen-to-carbon ratio
220 (H/C)) and some specific fragment ions. The average oxidation state of carbon (OSc =
221 $2 \times O/C - H/C$) was used to index the oxidation degree of aqSOA. 10 mg/L ammonium
222 sulfate was added into the solution as an internal standard for quantifying SOA mass
223 concentration. The aqSOA mass yield was calculated as follows:

删除[bess_je]: of aqSOA composition and mass yield

$$224 \text{aqSOA yield} = \frac{[Org]_t - [Org]_0}{[WSOC]_0 - [WSOC]_t} = \frac{[Org]_t \times \frac{[SO_4^{2-}]_t}{[SO_4^{2-}]_{AMS,t}} - [Org]_0 \times \frac{[SO_4^{2-}]_0}{[SO_4^{2-}]_{AMS,0}}}{([WSOC]_0 - [WSOC]_t) \times M/12} \quad (5)$$

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227 Where $[SO_4^{2-}]_t$ and $[SO_4^{2-}]_0$ denote sulfate concentrations (mg/L) in the solution at
228 irradiation time t and zero, respectively. Here, $[SO_4^{2-}]_t$ was equal to $[SO_4^{2-}]_0$ assuming
229 sulfate was not loss during irradiation. The $[Org]$ and $[SO_4^{2-}]_{AMS}$ denote the apparent
230 concentrations of aqSOA and sulfate measured by HR-AMS. $[WSOC]_t$ and $[WSOC]_0$
231 were WSOC concentrations in the solution measured by TOC at irradiation time t and
232 zero, respectively. M represents the averaged molecular weight of mixed solution
233 which can be estimated by FT-ICR MS.

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234 2.7 ROS determination based on electron paramagnetic resonance

235 Electron paramagnetic resonance (EPR) spectroscopy (Bruker EMXnano,
236 Germany) was used to detect ROS. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) and
237 2,2,6,6-tetramethylpiperidine (TEMP) were used as spin-trapping agents for $\cdot\text{OH}$
238 and $^1\text{O}_2$ to identify the DMPO-OH adducts (1:2:2:1) and the TEMPO adducts (1:1:1),
239 respectively (Hu et al., 2025; Wang et al, 2020). The 10 mL of aqueous extracts were
240 diluted into 100 mL using deionized water and pH was adjusted at 5.0 ± 0.1 with 0.1
241 M H_2SO_4 solutions. Then 100 mM of two spin-trapping agents were added into the 50
242 mL of acidified aerosol extract solutions. After photodegradation of smoke extracts,
243 200 μL of solutions were transferred from the reaction solutions and immediately
244 analyzed by EPR. The EPR parameters were set as following: modulation frequency
245 of 100 kHz; center field of 3460 G, modulation amplitude of 1G, microwave power of
246 25 mW, sweep width of 200 G, sweep time of 150 s, number of scans of 20.

247 **3 Results and discussion**

248 **3.1 Comparison of fresh coal and maize smoke WSOM**

249 Fig. 1 showed the reconstructed FT-ICR mass spectra of WSOM for two fresh
250 extracts samples. Based on the intensity of each negative ion, the average molecular
251 formulas for coal and maize smoke extracts calculated as $\text{C}_{18.0}\text{H}_{24.0}\text{O}_{6.9}\text{N}_{0.90}\text{S}_{0.41}$ and
252 $\text{C}_{21.0}\text{H}_{21.7}\text{O}_{7.4}\text{N}_{0.86}\text{S}_{0.04}$, respectively, showing higher C in maize smoke extracts,
253 consistent with previous finding (Fan et al., 2016). In this study, these identified
254 molecular formulas were classified into four main compound groups based on their
255 compositions: CHO, CHON, CHOS, and CHONS. The relative abundances of the
256 four groups were determined by normalizing the magnitude of each peak to the total

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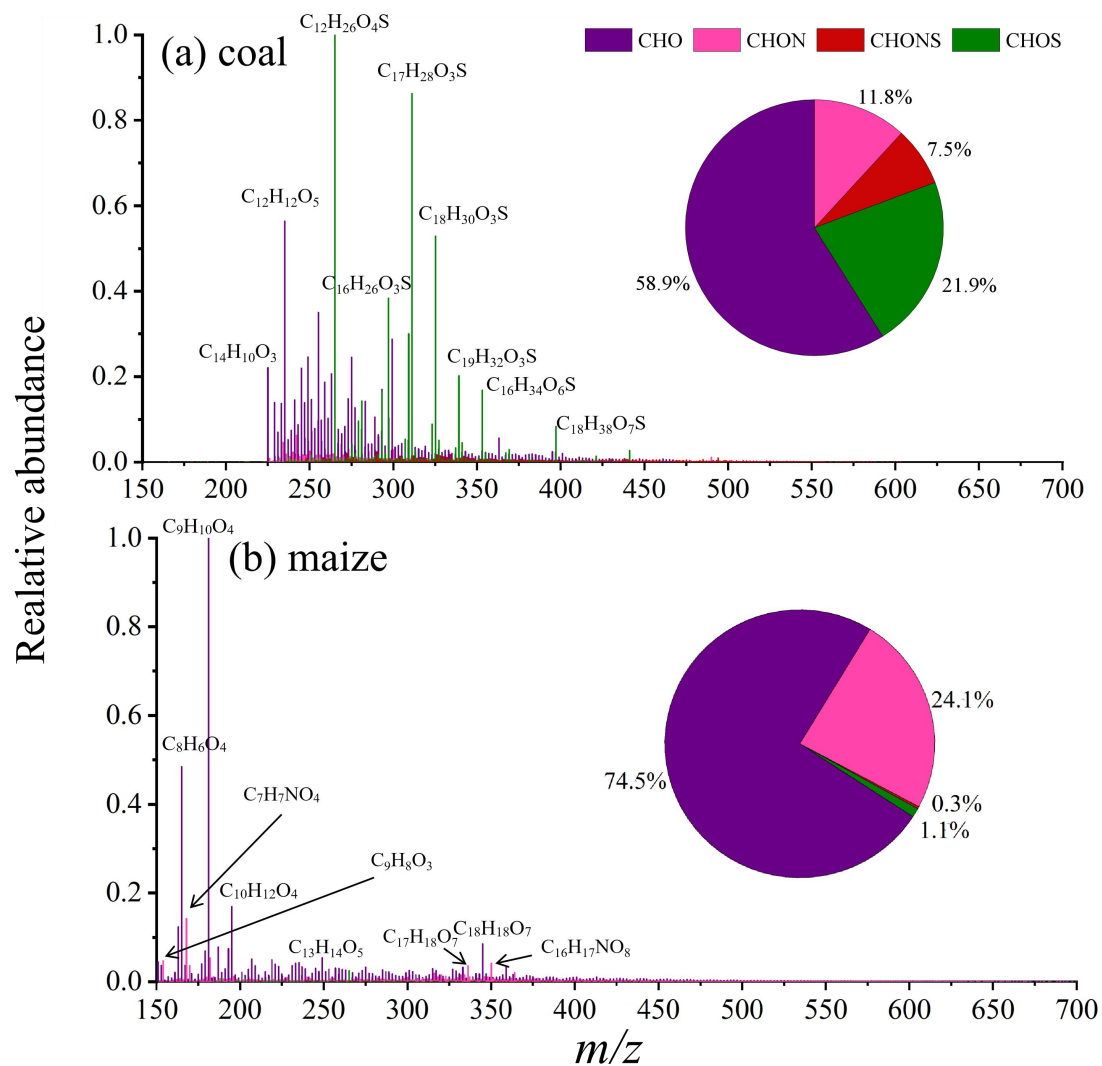
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257 magnitude of all identified peaks. Most peaks were located within the m/z range of
258 200–400. The greatest peak magnitudes were mainly distributed within the m/z range
259 of 250–350. Distinct peak distribution patterns were observed for both smoke extracts.
260 For example, several CHOS compounds with high relative abundance, such as
261 $C_{12}H_{26}O_4S$, $C_{17}H_{28}O_3S$, $C_{18}H_{30}O_3S$, were identified in the coal smoke extract, whereas
262 the high-abundance CHO and CHON compounds, including $C_8H_{10}O_4$, $C_7H_7NO_4$, and
263 $C_{18}H_{18}O_7$ were predominant in the maize smoke extract. It should be noted that peak
264 magnitude is not indicative of a compound's concentration in a sample due to inherent
265 biases of C18 extractions and electrospray ionization efficiencies. _

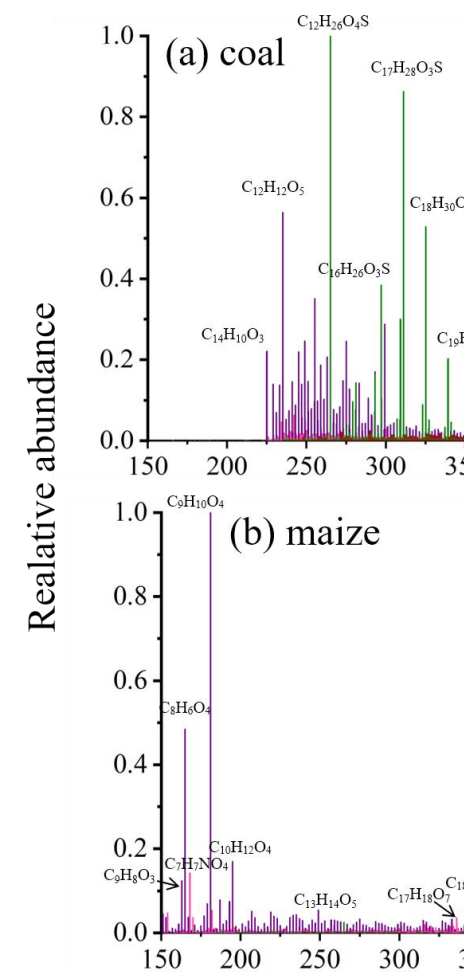
266 To better illustrate the differences in the \bullet OH oxidation behavior between the
267 two extracts, the concentrations of inorganic ions and transition metals (Fe and Cu) in
268 the fresh WSOM were also measured, as shown in Table S1. It can be seen that the
269 concentrations of Cl^- and NH_4^+ ions in maize were much higher than those in coal,
270 whereas the concentration of SO_4^{2-} ions in coal was higher than that in maize. During
271 the photochemical reaction, the concentrations of these ions showed little change. In
272 addition, the concentrations of Fe and Cu ions were very low, almost below the
273 detection limits of the instrument. These results indicate that the influence of ions on
274 the photochemical reaction can be neglected, especially that of Fe and Cu.

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275

276 **Fig. 1.** Reconstructed ESI(-) FT-ICR mass spectra of (a) coal and (b) maize smoke extracts

277 colored by formula groups. The inserted pie charts show the percentage of four formula groups by

278 intensity.

279

280 3.2 Optical properties during photooxidation of smoke extracts

281 3.2.1 Absorbance characteristics

282 Aqueous \bullet OH oxidation of two smoke extracts—involving both photolysis and

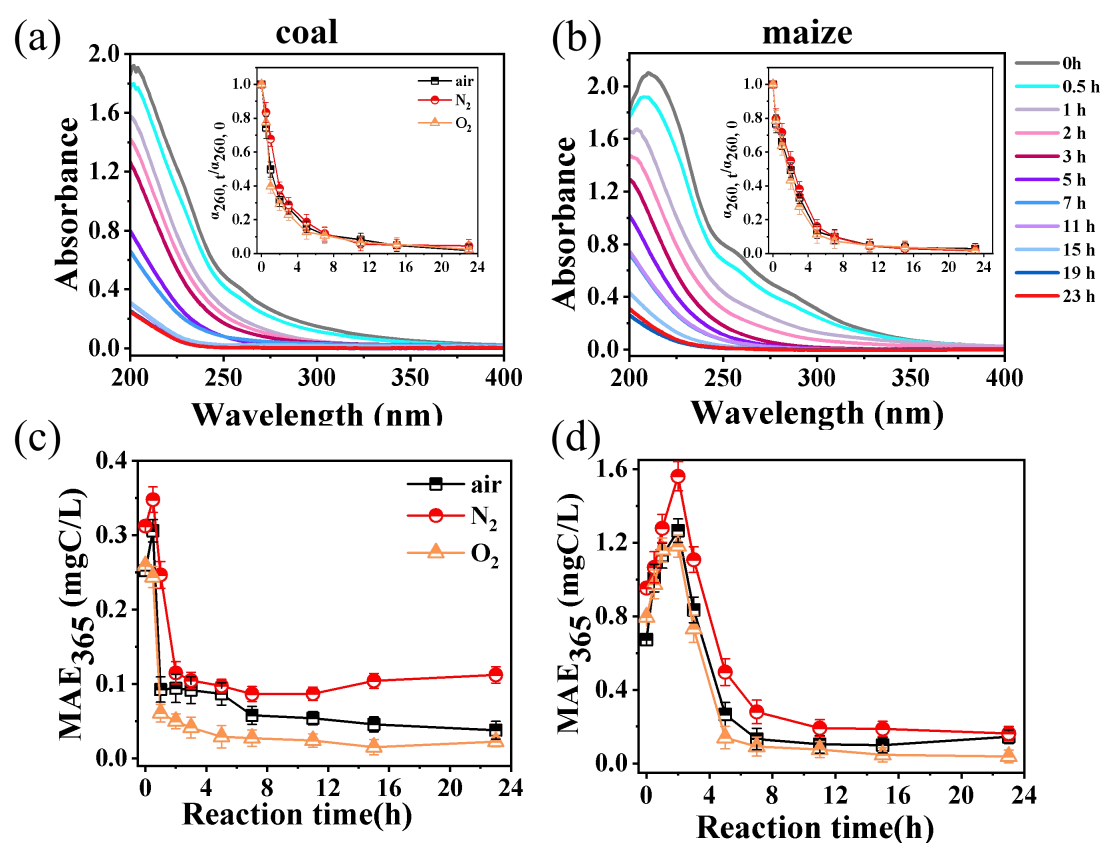
283 ROS oxidation reactions—can markedly alter their optical properties by degrading

284 existing chromophores or generating new light-absorbing compounds. Fig.2 (a, b)

285 shows the UV-vis absorbance spectra in the range of 200-500 nm of the reaction
286 solutions at varying irradiation time. Although the spectra were generally broad and
287 featureless, noticeable differences in the absorption intensity were observed between
288 coal and maize smoke. A distinct shoulder at 260 nm was observed in the spectra of
289 maize smoke WSOM, attributed to π - π^* transitions of unsaturated double bonds (e.g.,
290 C=C and C=O) (Li et al., 2021), indicating the presence of fulvic acid-like
291 chromophores. As the reaction progressed, overall decreases in absorbance (Fig. 2)
292 were observed for both smoke extracts, which can be ascribed to the degradation of 删除[bess_je]: types of
293 compounds containing carbonyl- and double bond groups. Tomaz et al. (2018)
294 similarly reported that aqueous α OH oxidation of complex BB mixtures led to rapid
295 depletion of phenolic compounds and formation of small organic acids. Consistent
296 with these findings, photobleaching (i.e. decrease in light absorbance) is the most
297 common effect observed upon irradiation of SOA or BrC in the aqueous phase (Jiang
298 et al., 2023). The decreased light absorption was likely due to competing processes,
299 including the formation of light-absorbing products and fragmentation yielding less
300 absorptive compounds. Study by Chen et al. (2025) on molecular structure-dependent 删除[bess_je]: The study
301 light absorption demonstrated that CHO compounds with low molecular weight and
302 high aromaticity are primarily responsible for absorption in the 200–300 nm range,
303 whereas CHON compounds (mainly nitroaromatics) and highly aliphatic structures
304 play a dominant role in absorption above 365 nm. However, the present results differ
305 from recent studies on aqueous SOA formation from the photooxidation of coal and
306 rice straw smoke WSOM, which reported photoenhancement at wavelength above 删除[bess_je]: burning

307 360 nm (Cao et al., 2025). Such discrepancies may be attributed to differences in light
 308 sources, \bullet OH concentrations, and the molecular composition of the smoke extracts.
 309 Clearly, different classes of compounds in smoke extracts exhibit distinct
 310 photochemical aging behavior, including photoenhancement, photobleaching or a
 311 combination of both.

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312
 313 **Fig. 2.** (a, b) The UV-vis absorption spectra under different irradiation time for coal and maize
 314 smoke extracts, and (c, d) MAE at 365 nm over photoaging time. The inset shows the change in
 315 absorbance at the wavelength of 260 nm compared to the spectra at time zero.

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316
 317 Changes in MAC₃₆₅ are commonly used to track chromophore evolution since
 318 different chromophores exhibit varying light-absorbing ability. Fig. 2(c, d) shows the
 319 variation of the MAC₃₆₅ over reaction time for both smoke extracts. For both smoke

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320 extracts, MAE₃₆₅ initially increased and then declined. The enhancement in
321 light-absorbing can be mainly ascribed to two factors (Jiang et al., 2021). First,
322 OH-addition to aromatic rings produces OH-rich compounds that act as chromophores
323 (Lei et al., 2024). Second, the formation of dimers and larger oligomers extends
324 π -conjugation, shifting absorption to longer wavelengths and enhancing light
325 absorption. Generally, increased functionalization and oligomerization increased light
326 absorption (Go et al., 2024; Vione et al., 2019). As the reaction proceeds, these
327 intermediate chromophores transform into smaller, ring-opened molecules with
328 weaker or negligible light absorption. The aqueous-phase photoaging of phenolic
329 SOA also showed that light-absorbing properties of oxidation products were strongly
330 time-dependent (Jiang et al., 2023). Additionally, photodegradation of WSOM can
331 generate more volatile products, and their evaporation may reduce WSOC (Fig. S1),
332 thereby influencing the light absorption per unit C mass. The final decrease in
333 MAE₃₆₅ can also be supported by the FT-ICR MS results (see Sect. 3.3). The observed
334 decrease in lignin-like fractions, together with reductions in DBE and AI values,
335 suggests the breakdown of these conjugated systems during aqueous photooxidation,
336 leading to a decline in MAE₃₆₅. Meanwhile, the formation of more saturated
337 compounds (e.g., lipid- and aliphatic-like species) further contributes to the decrease
338 in MAE₃₆₅. In addition, the formation of small oxygenated CHO species (e.g.,
339 carboxylic acids or CHO₂⁺ fragments from HR-AMS) with negligible absorbance at
340 365 nm dilutes the overall light-absorbing capacity. Another spectral parameter, E2/E3
341 (the ratio of absorbance at 250 nm to that at 365 nm), further characterizes these
342 changes. During the first hour of α OH oxidation, E2/E3 decreased from 16 to 8 for
343 coal smoke, indicating enrichment in high-molecular-weight chromophores with
344 stronger light-absorbing capability. However, it increased from 12 to 22 for maize

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fluorescence (Sect. 3.2.2).

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345 smoke extracts (Fig. S2). These contrasting E2/E3 trends highlight distinct molecular
346 transformations in WSOM for coal and maize smoke under α OH photooxidation,

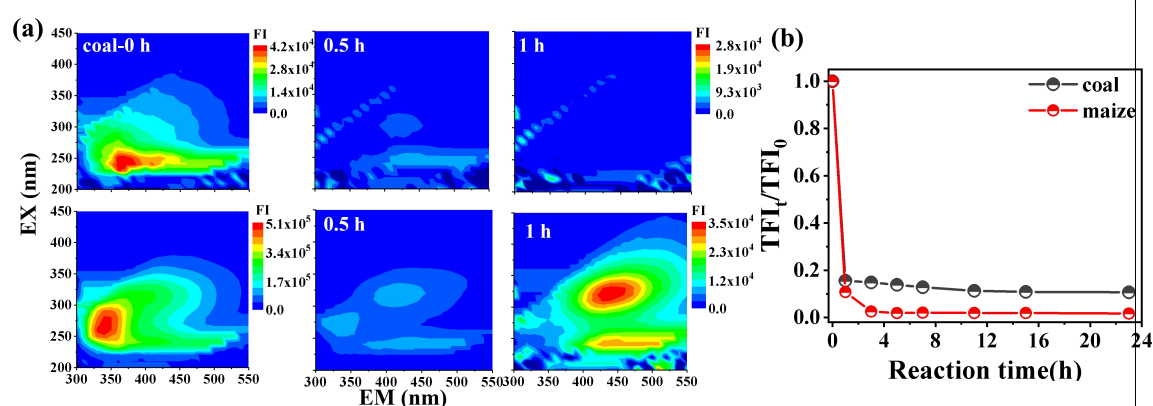
347 3.2.2 Fluorescence properties

348 Fluorescence spectra provide more detailed molecular information than UV-vis
349 spectra. For example, a red shift in the excitation–emission maximum typically
350 indicates increased aromaticity and higher molecular weight (Tang et al., 2020). Fig.
351 3a presents the EEM spectra of both smoke samples upon irradiation. We observed a
352 rapid decrease in the characteristic fluorescence peak (Ex/Em = 275/350 nm) within
353 the first hour of the reaction. Concurrently, two new fluorescence peaks emerged at
354 Ex/Em = 325/400–500 nm and 225/400–500 nm, indicating the formation of
355 humic-like chromophores. As the reaction progressed, the intensities of these newly
356 formed peaks gradually declined. Consistently, HULIS-C concentrations increased
357 during the initial 1–3 h for both smoke extracts, followed by a gradual decrease over
358 time (Fig. S3). As shown in Fig. 3b, the total fluorescence intensity (Ex = 250–450
359 nm, Em = 300–650 nm) decreased sharply within the first hour and then declined at a
360 slower rate thereafter.

361 The HIX, BIX and FI were further employed to evaluate the degree of
362 humification and freshness of organic matters. As suggested by Wu et al. (2021), an
363 increased in HIX accompanied by decrease in BIX and FI can serve as indicators of
364 enhanced oxidation of atmospheric WSOC. As shown in Fig. S4, the HIX value
365 increased during the first hour and then decreased, suggesting that the formation of
366 humic-like substances initially exceeded their subsequent degradation. Conversely, FI

367 and BIX values decreased at the early stage of oxidation for both smoke samples (Fig.
 368 S4). In general, greater humification is associated with lower protein content,
 369 primarily due to a reduction in carbon-hydrogen compounds and a red shift in the
 370 fluorescence emission wavelength of more humified molecules. Conversely, a higher
 371 BIX indicates a higher contribution from protein-like and amino acid components.

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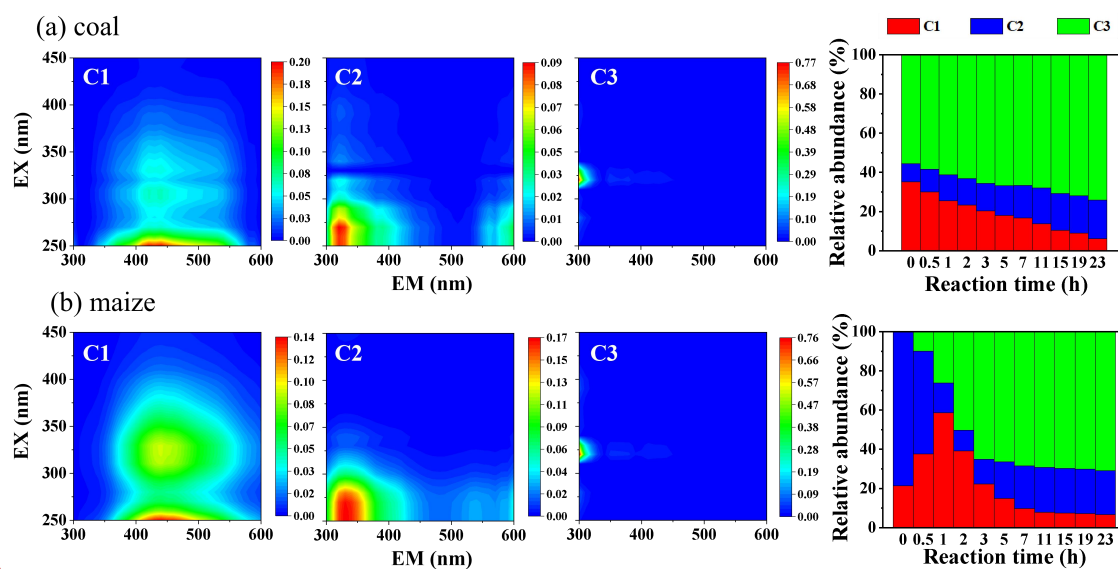


372
 373 **Fig. 3.** (a) Variation trend of EEM fluorescence spectra and (b) temporal profiles of total
 374 fluorescence intensity for two smoke extracts.

375
 376 The PARAFAC model identified three underlying fluorescent components,
 377 including one humic-like components (C1) and two protein-like component (C2 and
 378 C3) (Fig. 3). Component C1 is considered to be a humic-related substance,
 379 characterized by two peaks at Ex/ Em=230/400–500 nm and 300/400-500 nm (Huang
 380 et al., 2025). C2 displays peaks at Ex/Em=250-300/300-350 nm, which can be
 381 attributed to tyrosine-like components. C3 (Ex/Em=325/300 nm) is likely link to
 382 tryptophan-like components. As shown in Fig. 4, the proportion of C1-C3 in both
 383 maize and coal WSOM varied dynamically throughout photochemical processes. For
 384 coal WSOM, C1 fraction decreased, whereas C2 and C3 increased. In contrast, for

385 maize WSOM, C2 gradually transformed into C1 at the first hour, resulting in
386 opposite trends between the two components. This transformation likely reflects the
387 formation of more oxygenated humic-like substances via OH-functionalization at the
388 early stage, consistent with change trends of Hulis-C for maize smoke extracts (Fig.
389 S3). This interpretation can be further confirmed by the increase in HIX values for
390 maize smoke during the first hour of photooxidation (Fig. S4 c).

391 For both smoke WSOM samples, the C3 component exhibited a gradual increase
392 over time. The findings are in accordance with other's study on the photooxidation of
393 WSOC emitted from rice straw combustion (Zhang et al., 2021). The stronger
394 fluorescence intensity observed at Ex/Em=325/300 nm may correspond to low-ring
395 PAHs and their derivatives, which are known to be produced in abundance during
396 biomass pyrolysis or burning (Mahamuni et al., 2020). Overall, the EEM components
397 varied depending on the types of smoke-derived WSOM.



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398
399 **Fig. 4.** Three fluorescent components (C1-C3) of the smoke extracts identified by the
400 EEM-PARAFAC model and variations in the relative contributions of each PARAFAC
401 component of (a) coal and (b) maize smoke extracts with photoaging time.

402

403 3.3 Molecular composition of WSOM via FT-ICR MS

404 The intensity weighted average values of various molecular
405 parameters—including molecular weight (MW), elemental ratios (H/C and O/C), DBE,
406 AI—for maize and coal smoke extracts before and after photoaging were summarized
407 in Table 1. As listed in Table 1, a total number of 5596 and 5107 molecular formulas
408 were identified for fresh coal and maize extracts, respectively, within the m/z range of
409 100-600, indicating the complicated molecular compositions of WSOM. For coal
410 WSOM, the MW decreased slightly 313 g/mol in the fresh sample to 296 and 288
411 after 11 h and 23 h photooxidation, respectively. The MW for maize remained nearly
412 unchanged during OH-photooxidation. The dominant species in both smoke extracts
413 were CHO and CHON compounds, with higher abundance observed in maize than in
414 coal smoke extract (Fig. 5). Molecular composition analysis further revealed that
415 maize smoke WSOM was largely composed of CHO and CHON, together accounting
416 for 98.6% of the total peak area. CHO compounds constituted more than half of all
417 identified molecular formulas in both WSOM samples (74.5% for maize and 58.9%
418 for coal). In contrast, S-containing compounds (CHOS and CHONS) were much more
419 abundant in coal smoke extracts (29.4% in total) than in maize (1.4% in total).
420 Similarly, previous studies reported that the fractions of S-containing CHOS and
421 CHONS species in crop-derived WSOM were relatively low (3-9% in peak area) (Li
422 et al., 2024). Interestingly, S-containing compounds in coal smoke decreased by
423 nearly 50% after photodegradation, whereas their abundance increased markedly in
424 maize smoke extracts. Meanwhile, the proportion of CHON compounds in coal
425 smoke increased, under photoaging, which may be attributed to the photochemical
426 transformation of CHONS species and/or the oxidation of reduced CHN compounds.
427 Conversely, the CHON proportion in maize smoke decreases with reaction time,

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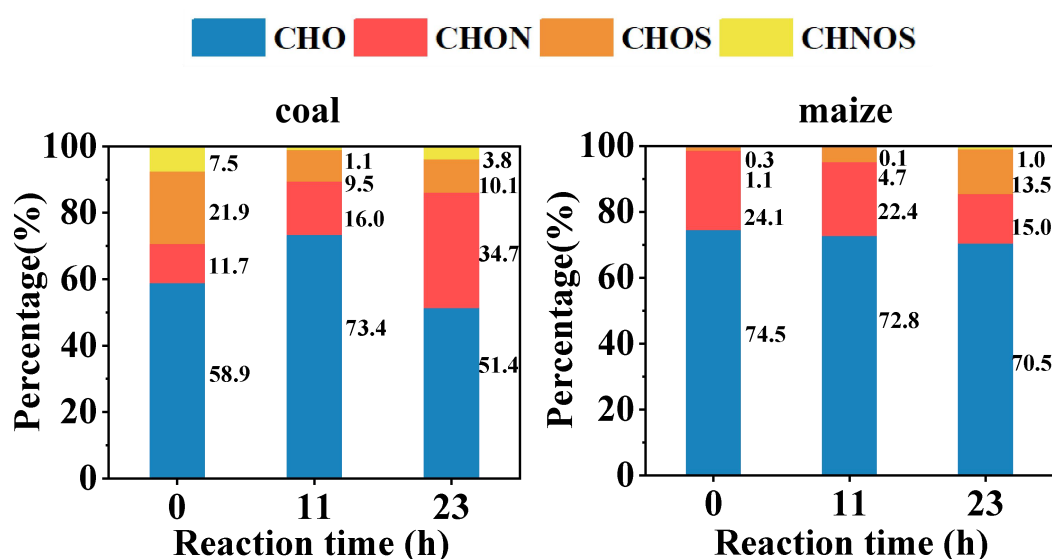
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428 likely due to the progressive degradation of nitroaromatic compounds commonly
 429 present in biomass burning emissions (Lin et al., 2016).



430
 431 **Fig. 5.** Change of relative abundance fraction of four groups (CHO, CHON, CHOS, and CHONS)
 432 with reaction time in both smoke extracts.

433 The molecular-level parameters are summarized in Table 1. DBE values ranged
 434 from 2 to 9 for coal-smoke WSOM and from 2 to 11 for maize-smoke WSOM. The
 435 degree of unsaturation and aromaticity of molecular formulas can be evaluated using
 436 the H/C ratio and DBE values, with lower H/C ratios and higher DBE indicating
 437 greater unsaturation and, to some extent, stronger aromatic character. As shown in
 438 Table 1, after 23 h of photooxidation, aged WSOM exhibited higher H/C ratios (1.75
 439 vs. 1.32 for coal; 1.68 vs. 1.02 for maize), lower DBE values (3.85 vs. 7.12 for coal;
 440 4.08 vs. 8.99 for maize), and reduced AI values (0.16 vs. 0.31 for coal; 0.16 vs. 0.48
 441 for maize) compared to the fresh samples. These concurrent changes consistently
 442 indicate the breakdown of aromatic structures and an overall shift toward more
 443 saturated compounds. This trend agrees with previous findings from dark aqueous

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444 OH oxidation of BB smoke WSOC reported by Fan et al. (2024). ▾

445 At the molecular-class level, CHON compounds in maize smoke initially exhibit a
446 relatively high average molecular weight (MW, 329.45 g/mol) and DBE (10.52).
447 Upon photolysis, the average MW decreases to 301.07 g/mol (11 h) and 296.44 g/mol
448 (23 h), while the DBE declines to 6.59 and 4.14, respectively. These changes reflect
449 the progressive breakdown of conjugated structures and a corresponding reduction in
450 aromaticity, consistent with the observed decrease in light absorbance (Fig.2 b). For
451 coal smoke, a considerable fraction of CHONS species undergoes transformation into
452 CHON compounds with lower aromaticity and DBE during photolysis. This
453 conversion increases the relative abundance of CHON species while contributing to a
454 decrease in overall molecular weight. In addition, the MW of CHO compounds in
455 coal smoke decreases progressively with photolysis. In contrast, maize-smoke WSOM
456 is dominated by CHO compounds, whose MW remains relatively unchanged during
457 photolysis, resulting in only minor variation in the bulk molecular weight. This
458 contrast primarily reflects differences in the initial WSOC compositions between coal
459 and maize smoke. Overall, the marked decreases in AI and DBE for CHON
460 compounds in both smokes indicate substantial loss of aromaticity, which in turn
461 contributes to the reduction in light absorption.

462 Additionally, the O/C increased from 0.38 to 0.45 for coal and from 0.40 to 0.55
463 after 11 h of oxidation, followed by a decrease to 0.27 and 0.25 at 23 h, respectively.
464 This trend indicates a transformation from OH-functionalization to fragmentation as
465 photooxidation progressed. A decrease in DBE per carbon (DBE/C) was observed
466 after 23 h of photodegradation—from 0.45 to 0.25 for coal and 0.62 to 0.27 for

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467 maize—further confirming the transformation of refractory aromatic-condensed
 468 structures into more polar and readily degradable small molecules. Fig. S5 shows the
 469 relationship between DBE values and C atom numbers for four compound groups
 470 identified by FT-ICR MS.

471 **Table 1** Intensity-weighted average molecular parameters (MW, elemental ratios, DBE, DBE/C,
 472 AI) of coal and maize smoke WSOM before and after ·OH photooxidation

Sample	Time	Elemental composition	Formulas number	MW (g/mol)	DBE	AI	O/C	H/C	DBE/C
coal	0 h	Total	5596	312.98	7.12	0.31	0.38	1.32	0.45
		CHO	1728	300.23	8.16	0.38	0.36	1.16	0.52
		CHON	1695	323.12	8.77	0.43	0.49	1.25	0.54
		CHOS	702	310.03	3.60	0.10	0.31	1.74	0.23
		CHONS	1471	406.27	6.61	0.19	0.55	1.48	0.41
	11 h	Total	5157	296.35	4.58	0.17	0.45	1.57	0.34
		CHO	2066	286.35	4.61	0.16	0.47	1.54	0.35
		CHON	2029	312.31	4.10	0.16	0.40	1.68	0.31
		CHOS	816	343.04	4.93	0.16	0.29	1.62	0.29
		CHONS	246	329.73	6.45	1.01	0.86	1.63	0.54
	23 h	Total	5072	288.32	3.85	0.16	0.27	1.75	0.25
		CHO	1348	262.69	4.04	0.15	0.26	1.66	0.28
		CHON	1970	304.36	2.03	0.07	0.25	1.99	0.14
		CHOS	723	313.19	4.80	0.17	0.31	1.67	0.27
		CHONS	1031	398.63	7.04	0.33	0.52	1.63	0.39

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	Total	5107	286.90	8.99	0.48	0.40	1.02	0.62	
	CHO	2143	273.62	8.56	0.46	0.40	1.02	0.61	
0 h	CHON	2772	329.45	10.52	0.54	0.40	0.98	0.66	
	CHOS	107	248.21	4.61	0.22	0.46	1.37	0.47	
	CHONS	85	317.32	7.31	0.28	0.56	1.13	0.61	
	Total	6027	288.84	5.44	0.21	0.55	1.40	0.44	
	CHO	2643	283.95	5.19	0.19	0.56	1.41	0.42	
maize	11 h	CHON	2954	301.07	6.59	0.30	0.57	1.29	0.54
	CHOS	395	305.41	3.69	0.12	0.35	1.83	0.20	
	CHONS	35	317.42	10.37	0.45	0.23	1.19	0.54	
	Total	5147	285.81	4.08	0.16	0.25	1.68	0.27	
	CHO	2647	277.01	4.20	0.16	0.23	1.65	0.27	
	23 h	CHON	1995	296.44	4.14	0.19	0.28	1.69	0.30
	CHOS	400	312.24	2.94	0.09	0.34	1.86	0.18	
	CHONS	105	393.70	10.63	1.03	0.49	1.11	0.67	

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474 The van Krevelen diagram (Fig. 6), which plots the O/C ratio as the x-axis and
 475 the H/C ratio on the y-axis, was used to elucidate the molecular distribution. For
 476 clarity, the corresponding detailed values were listed in Table S2. Lignin-like
 477 compounds dominated both coal and maize smoke WSOM, accounting for 58.2% and
 478 93.1% of total intensity, respectively, indicating a greater abundance of phenolic
 479 organic species in maize smoke. Previous study also showed that CHO formulas were
 480 mainly lignin-pyrolysis products (Song et al., 2018). After photoaging, the lignin-like

481 fraction decreased significantly, reflecting the degradation of aromatic phenolic
482 species. Given that most lignin-like compounds possess strong light-absorbing
483 properties, their decomposition directly contributed to the observed decrease in
484 absorbance. In contrast, the intensity of saturated compounds (sum of lipids and
485 aliphatic components) increased substantially after OH-induced photooxidation, from
486 33.8 % to 51.2% at 23 h for coal and from 2.4% to 69.8 % for maize. These
487 observations suggest a significant increase in saturated aliphatic and O-enriched
488 compounds after \bullet OH photooxidation.

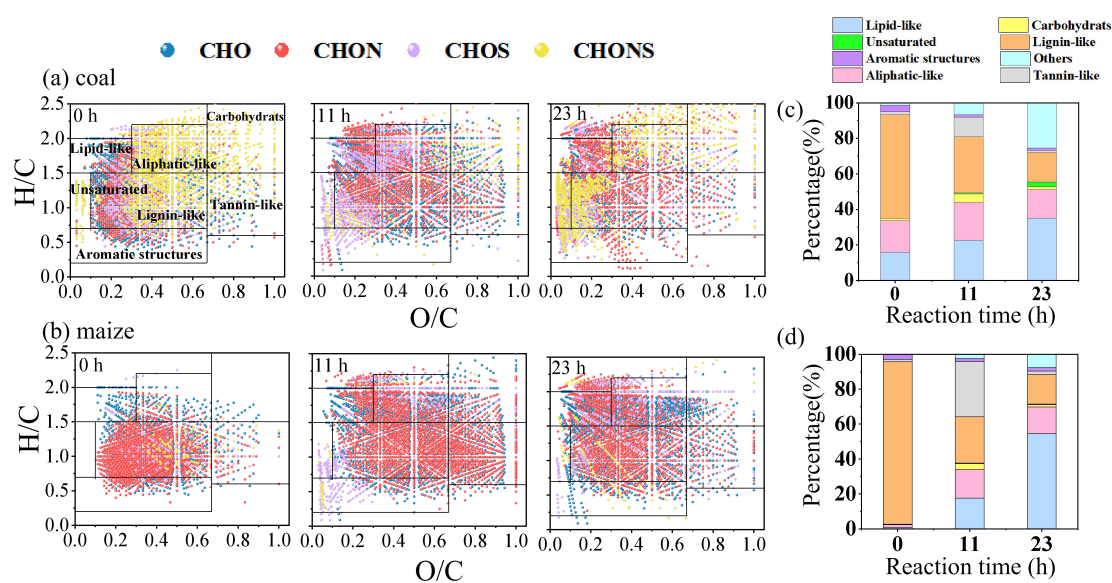
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489 As listed in Table S2, the initial increase followed by a decrease (from 11.2% to
490 1.1% for coal and 31.8% to 2.1% for maize smoke) in tannin-like compounds
491 suggests that radical coupling, condensation, or addition reactions likely occurred
492 during the early stage of the reaction, leading to a higher O/C ratio at 11 h compared
493 to the fresh sample.

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494 Condensed aromatic molecules, characterized by low H/C and O/C ratios but
495 high AI, showed a slight decrease with photoaging, indicating the partial degradation
496 of highly aromatic structures. Overall, the reduction in aromatic and lignin-like
497 compounds aligns with the observed decline in the light-absorbing properties (see
498 Sect. 3.2.1). In all, aromatic and lignin-like compounds were continuously
499 transformed into lipid- and aliphatic-like compounds. During the initial stage (first 5
500 h), carbohydrate-like substance such as oxalate were generated (Fig. S6), but their
501 abundance subsequently decreased, consistent with the pH variation that first declined
502 (initial 3 h) and then increased again (Fig. S7). The formation of carboxylic acids can
503 be further confirmed later by identifying their characteristic fragment ions using



505

506 **Fig. 6.** (a, b) Van Krevelen diagrams of four groups (CHO, CHNO, CHOS, and CHNOS) and (c, d)

507 Intensity-weighted fractions of seven major molecular classes. Saturated compounds represent the

508 sum of lipid-like and aliphatic components. Unsaturated represents unsaturated hydrocarbons.

509

510 To further elucidate the photooxidation behaviors of both smoke extracts, the

511 number proportions of resistant, degraded and newly produced molecules were

512 summarized in Table S3. After 11 h of irradiation, 55.1 % and 58.2% of the total

513 formulas in fresh coal and maize, were degraded, resulting in 51.3% and 64.6% newly

514 formed formulas. From 11 h to 23 h, the numbers of newly produced and degraded

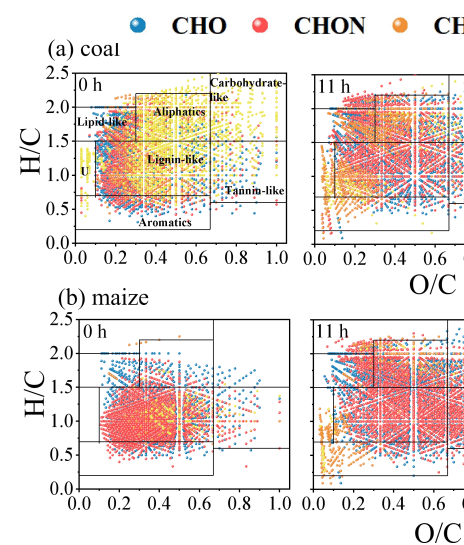
515 molecules increased slightly for coal but decreased for maize. Fig. 7 illustrates the

516 O/C vs. H/C distributions of degraded and newly formed compounds after 11 h and 23

517 h of photodegradation. For coal, most degraded compounds were located in high O/C

518 regions, whereas some newly formed species with much lower O/C and higher H/C

519 were likely associated with unsaturated hydrocarbons and lipid-like species. In



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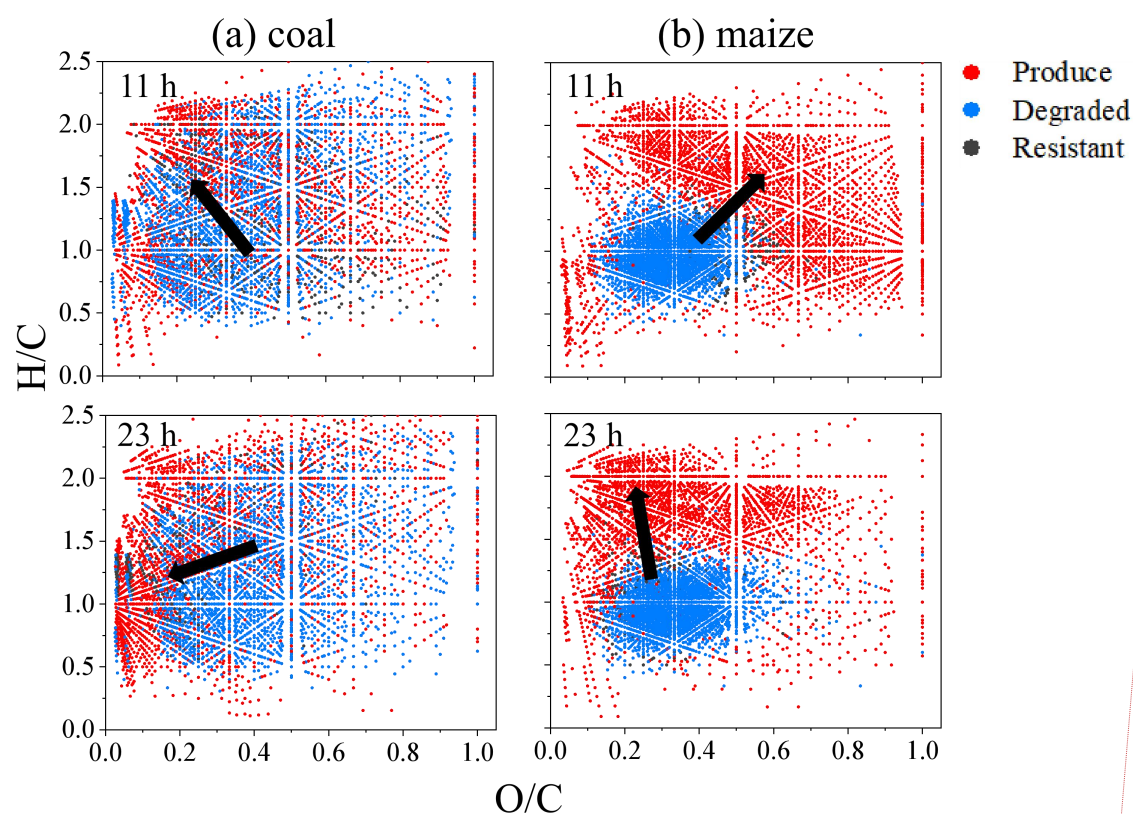
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520 contrast, maize exhibited a marked shift from low to high O/C and H/C compounds at
521 11 h, resulting in an increase in average O/C ratio. This trend suggests that maize
522 compounds mainly underwent functionalization during the first stage—introducing
523 oxygen-containing groups without breaking the carbon skeleton, thereby increasing
524 O/C and slightly lowering or maintaining H/C. The shift toward higher O/C ratios in
525 the van Krevelen diagram further supports the progression from aromatic to more
526 oxygenated and saturated compounds for maize smoke WSOM.

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527 Overall, these results reveal distinct degradation pathways and product
528 characteristics for coal and maize smoke extracts.

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529 **Fig. 7.** Van Krevelen diagrams of resistant, degraded and produced formulas in WSOM derived
530 from (a) coal and (b) maize burning before and after OH photooxidation.
531

532 3.4 AqSOA composition and mass yield

533 The aqSOA spectra exhibited higher mass fractions of $C_xH_y^+$ and $C_xH_yO_1^+$
534 ions but lower fractions of $C_xH_yN_p^+$ and $C_xH_yO_xN_p^+$ ions (Fig. 8). For corn-derived
535 aqSOA, the fractions of $C_xH_y^+$ and $C_xH_yO_1^+$ both decreased by approximately 10%
536 with increasing photolysis time, while $C_xH_yO_2^+$ increased substantially from 15.95%
537 to 29.96% after 23 h of photoreaction. In contrast, for coal-derived aqSOA, the
538 fraction of $C_xH_yO_1^+$ increased with irradiation time, while no corresponding increase
539 in $C_xH_yO_2^+$ was observed. This suggests that the overall oxidation degree of
540 coal-derived aqSOA did not increase significantly relative to that prior to irradiation.

541 Table S4 summarizes the chemical properties, mass concentration and yield of
542 the formed aqSOA and their evolution during the photoreaction. During the first 5 -7
543 h, both f_{44} and OS_C values increased, indicating a progressive enhancement in the
544 oxidation state of aqSOA for both samples. In contrast, the H/C ratio exhibited only
545 minor changes throughout the reaction, suggesting relatively stable bulk hydrogen
546 content despite ongoing oxidation. A comparison between the two systems further
547 reveals that maize-derived aqSOA undergoes a more pronounced increase in
548 oxidation at the early stage, likely driven by functionalization reactions. As
549 photochemical processing continues, however, a slight decline in oxidation is
550 observed, which can be attributed to fragmentation processes. This trend is less
551 evident in coal-derived aqSOA, highlighting differences in their underlying
552 transformation mechanisms. Notably, the significantly higher O/C ratios and OS_C of
553 maize-derived aqSOA compared to those of the precursors suggest that aqueous-phase
554 processing can serve as an effective source of oxygenated SOA in regions influenced
555 by biomass burning emissions. The value of f_{43} remained relatively low value (less
556 than 0.1) and is therefore not discussed further.

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557 For coal samples, the aqSOA mass concentration ranged from 50.77 mg/L to
558 126.95 mg/L. It reached a minimum at 11 h and subsequently increased to 126.95
559 mg/L at 23 h. Correspondingly, the aqSOA mass yield peaked at 148.44% at 1 h,
560 continuously decreased to 1.87% within 9 h, and then increased again to 33.91% at 23
561 h. The aqSOA mass yield of maize was significantly lower (less than 10%) than that
562 of coal samples, indicating that coal sample is more efficient at generating
563 low-volatility species compared to maize. The possible reasons why coal-derived
564 aqSOA is higher than that from maize are as follows. First, the fresh coal-derived
565 CHOS compounds are dominated by species such as C₁₇H₂₈O₃S and C₁₈H₃₀O₃S,
566 which are mainly organosulfates. These compounds have relatively high saturation
567 and stability, and undergo little change upon photolysis, resulting in a high SOA mass
568 yield measured by HR-AMS. In contrast, maize-derived WSOM is primarily
569 composed of lignin-like substances with high DBE values, which are more susceptible
570 to OH functionalization, forming saturated fatty acids or polyhydroxy acids (e.g.,
571 C₉H₁₈O₆ and C₉H₁₀O₇). These products can further undergo fragmentation into
572 smaller, more volatile products (e.g., low-molecular-weight acids), leading to a lower
573 aqSOA mass yield.

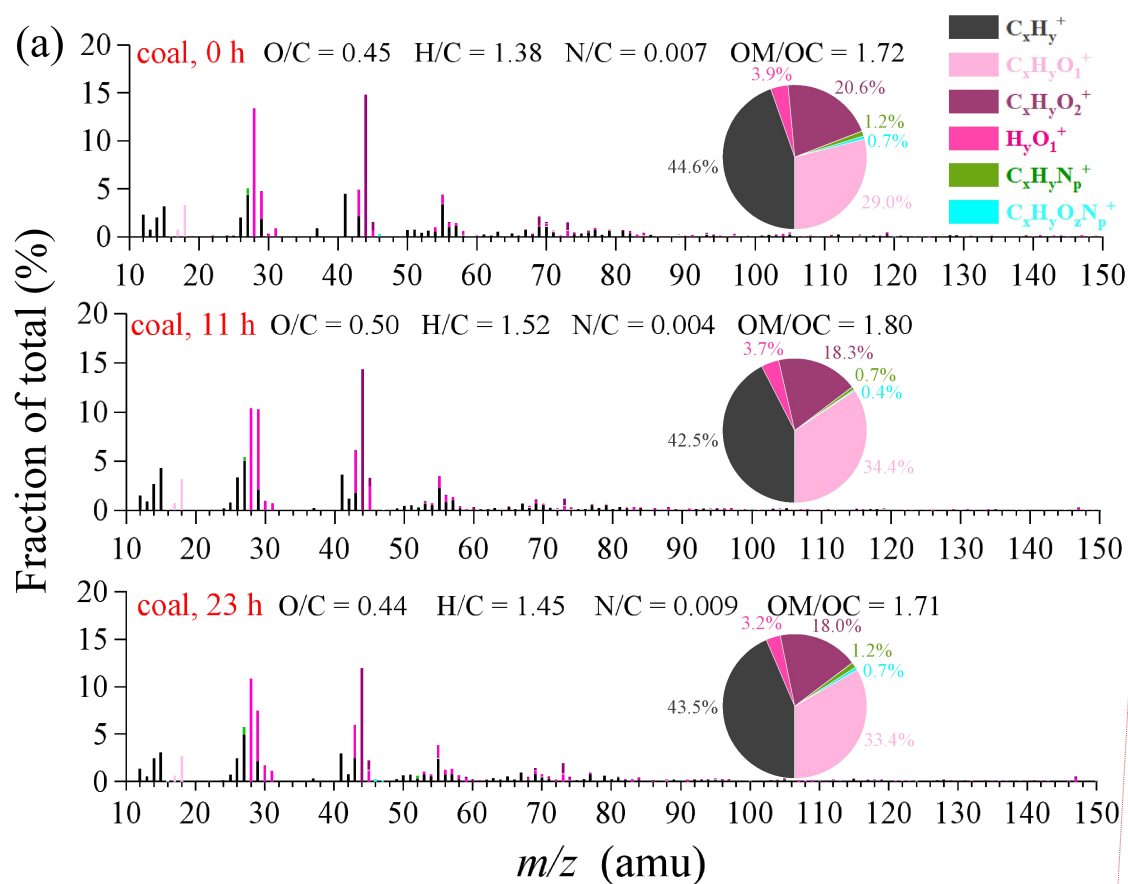
574 The significant formation of carboxylic acids during the first 9 h of photoreaction
575 is further evidenced by the Van Krevelen diagram (H/C versus O/C), in which aqSOA
576 evolves along a slope of approximately -1 throughout the photooxidation process (Fig.
577 S8). Consistently, the CHO₂[±] ion in the aqSOA AMS spectra—commonly used as a
578 tracer for carboxylic functional groups—exhibits a continuous increase during the
579 first 5 h of photoreaction (Fig. S9). After 3–9 h of reaction, the concentration of
580 CHO₂[±] decreases, accompanied by a decline in *f*₄₄. A plausible explanation is the

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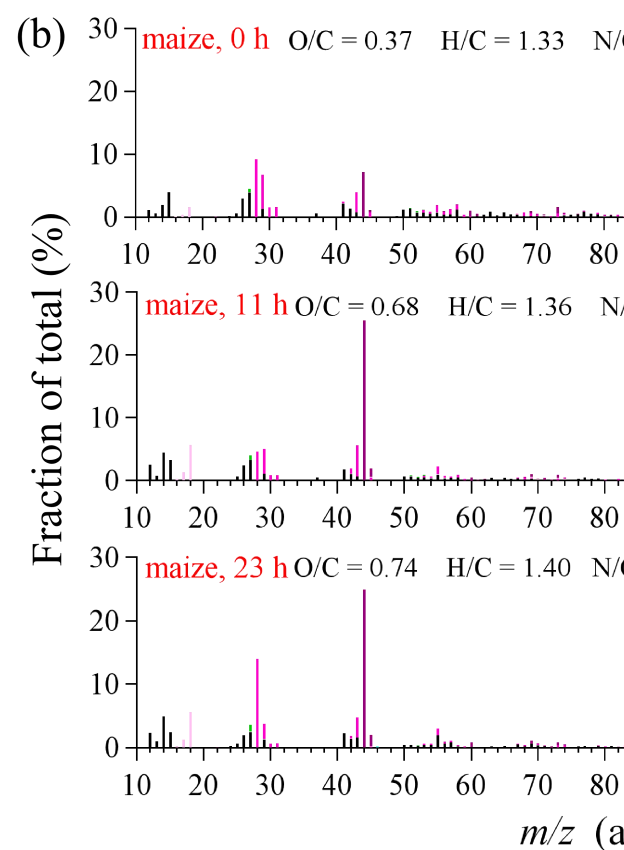
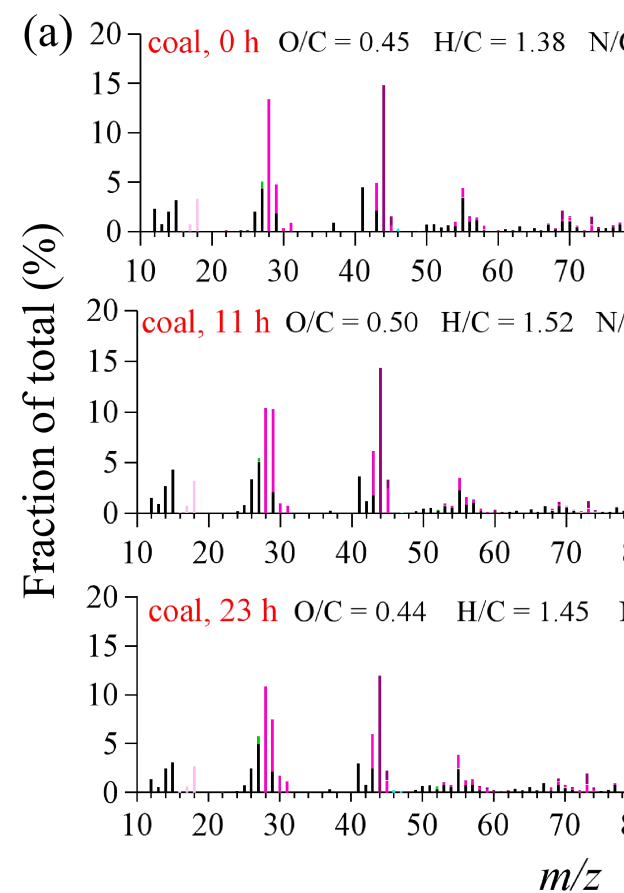
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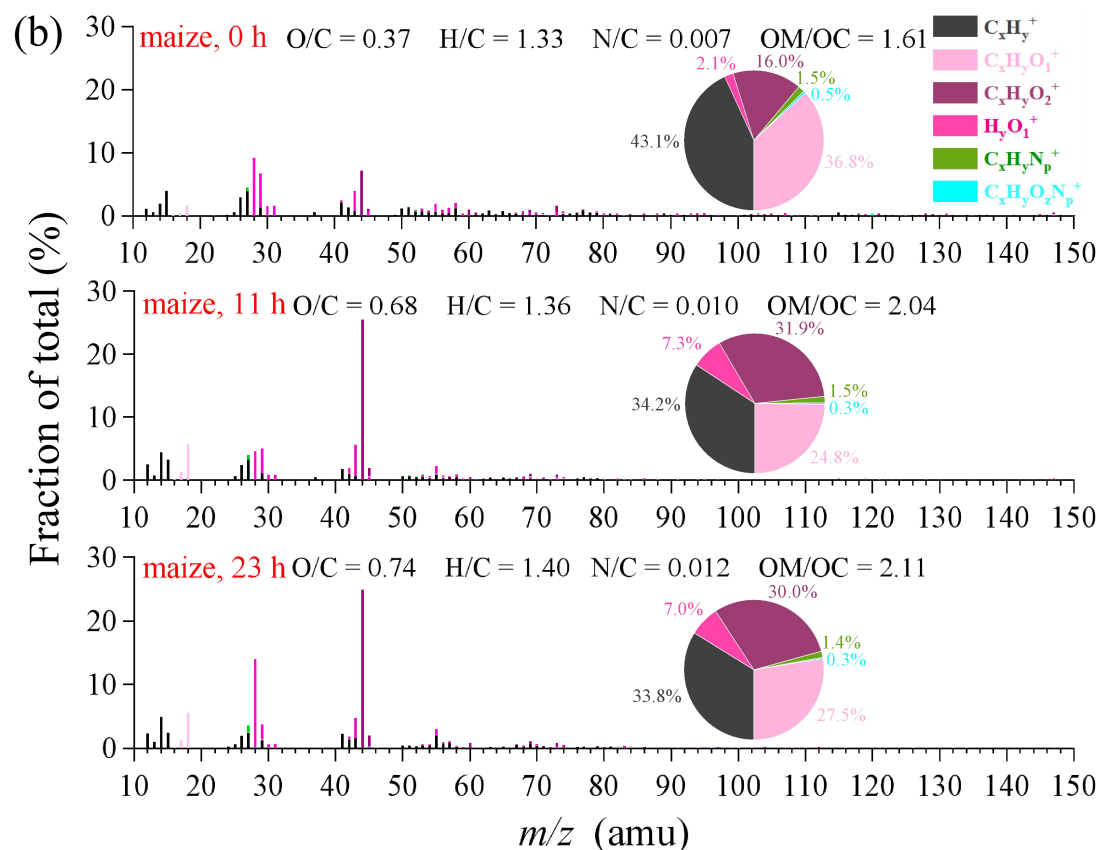
581 occurrence of fragmentation reactions, during which the oxidation products initially
 582 formed through oligomerization or functionalization decompose into smaller, more
 583 oxidized species. This trend has also been reported in previous studies on the
 584 photooxidation of phenolic carbonyls (Jiang et al., 2021).



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586

587 **Fig. 8.** High-resolution MS profiles for aqSOA products at 0 h, 11h and 23h for (a)coal and
 588 maize. The peaks in the mass spectra are color-coded according to six ion categories: $C_xH_y^+$,
 589 $C_xH_yO_1^+$, $C_xH_yO_2^+$, $H_yO_1^+$, $C_xH_yN_p^+$ and $C_xH_yO_xN_p^+$ ions. The inserted pie charts denote the mass
 590 fraction of each ion family to the total MS.

591

592 3.5 DTT analysis

593 Aqueous photochemical aging of BB smoke can also alter its toxicity. The
 594 oxidative potential of the reaction solutions was evaluated using the dithiothreitol
 595 (DTT) assay, as described in our previous work (Ye et al., 2025). As shown in Fig. 9a,
 596 based on the DTT consumption rate (OP^{DTT}), OH-initiated photooxidation of smoke
 597 extracts led to an increase in OP^{DTT} during the first 1 h. Upon prolonged photoaging,
 598 the OP^{DTT} value decreased to $0.15 \mu\text{M DTT min}^{-1}$ after 23 h, slightly lower than the
 599 corresponding initial values. Previous research results also suggested that aqueous OH
 600 oxidation of WS-BBOA components generally leads to a final reduction in OP^{DTT}
 601 (Wong et al., 2019; Jiang and Jang, 2018) during prolong irradiation, consistent to our
 602 findings. The temporal variation pattern of OP^{DTT} is comparable to that observed for

603 aqueous oxidation of soybean straw extracts (Ye et al., 2025), but opposite to that of
604 4NC photodegradation (Lei et al., 2025). The DTT activity is likely associated with
605 light-absorbing and fluorescent substances containing large conjugated electron
606 systems, which can transfer electrons to participate in catalytic reaction, thereby
607 contributing to DTT activity (Chen et al., 2019). The reduction in DTT activity after
608 23 h agrees with the decrease of lignin-like and aromatic compounds revealed by
609 FT-ICR MS analysis.

610 Given that aqueous OH oxidation did not significantly reduce the total WSOC
611 concentrations, the decrease in OP^{DTT} is likely attributed to the formation of non- or
612 less DTT-active components. However, total WSOC decreased significantly upon
613 aging; consequently, the OP^{DTT} normalized by WSOC increased over irradiation time,
614 suggesting the possible formation of secondary toxic organic species during the aging
615 processes. Previous published studies have also showed that photochemical aging of
616 fresh particles can either enhance or diminish toxicity, depending on their sources and
617 oxidation conditions (Fang et al., 2024). To further characterize the ROS-generation
618 potential of WSOM from different combustion sources, we calculated the
619 WSOC-normalized DTT consumption rate ($\frac{OP^{DTT}}{WSOC}$, OP^{DTT} divided by WSOC). The
620 results showed that the mass-normalized DTT consumption rates gradually increased
621 and reached a plateau at 132 and 82 pmol/min/ μg for maize and coal smoke extracts,
622 respectively, similar to finding from Wong et al. (2019). These values are higher than
623 those reported for water extracts from $PM_{2.5}$ aerosol (22-68 pmol $\cdot\text{min}^{-1}\cdot\mu\text{g}^{-1}$) (Verma et
624 al., 2012). Based on the molecular-level differences after $\cdot\text{OH}$ photooxidation, the
625 reasons for the $\frac{OP^{DTT}}{WSOC}$ changes induced by OH-photolysis in coal and maize are
626 likely different. For coal, the increase in $\frac{OP^{DTT}}{WSOC}$ may primarily result from the

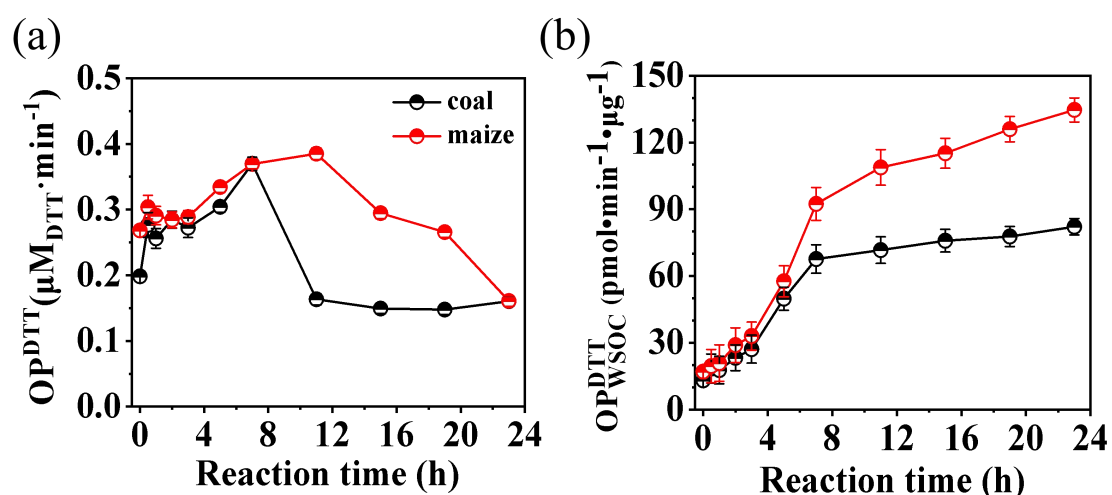
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627 formation of CHON compounds after photolysis, whereas for maize, the increase is
628 probably due to the production of more quinone species or OH addition products
629 during the reaction (Tang et al., 2025; Wong et al., 2019).

630 Unfortunately, due to the limitations of current analytical techniques, it remains
631 challenging or even impossible to attribute the observed DTT variation trends to
632 specific molecular species.



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633 **Fig. 9.** (a) Temporal evolution of DTT consumption rate and (b) WSOC-normalized DTT activity
634 for both smoke extracts during aqueous OH photooxidation.
635

636 3.6 ROS contribution and reaction mechanism

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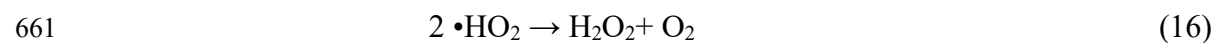
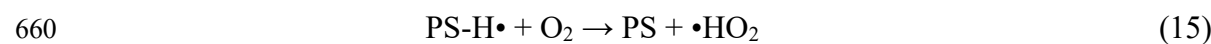
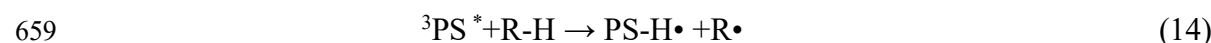
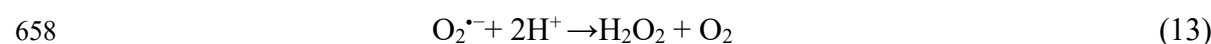
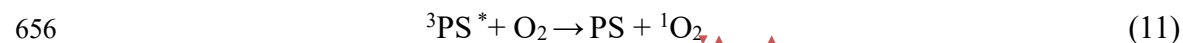
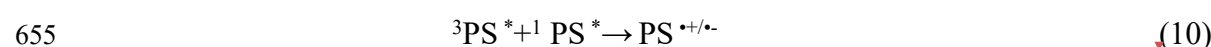
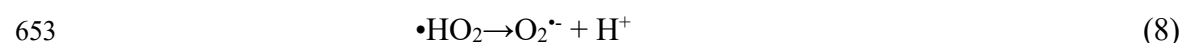
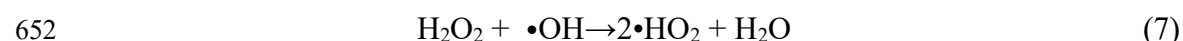
637 3.6.1 ROS concentration and relative contribution

638 Hydrogen peroxide can undergo photolysis to generate $\bullet\text{OH}$, which effectively
639 break down chromophores, thereby decreasing light absorption. The OH radicals can
640 oxidize most organic species, leading to a sharp decrease in both WSOC and
641 absorbance during the initial reaction stage.

642 According to previous studies (Arciva et al., 2022), when the concentration of the
643 BB mixture reaches 12 mg C/L, the concentration of photosensitizers in solution can

644 exceed several millimoles. This suggests that the smoke samples in the present study
 645 likely contains substantial amounts of photosensitizing compounds. Upon exposure to
 646 sunlight, these photosensitizer (denoted as PS) absorb photons and transition to their
 647 triplet excited state ($^3\text{PS}^*$). The excited triplet states can subsequently react with O_2 to
 648 produce various ROS, including $^1\text{O}_2$, superoxide ($\text{O}_2^{\cdot-}$), hydroperoxyl radical (HO_2^{\cdot}),
 649 and OH^{\cdot} , through H-abstracting, electron transfer and energy transfer processes.

650 These ROS species actively participate in subsequent photooxidation reactions.



662 According to method described in [Section 2.7](#), the steady-state concentrations of $\cdot\text{OH}$

663 (denoted as $[\cdot\text{OH}]_{\text{ss}}$) and $[\text{}^1\text{O}_2]$ (denoted as $[\text{}^1\text{O}_2]_{\text{ss}}$) were determined using [EPR](#). The

664 distinct 1:1:1 triplet EPR signal characteristic of $^1\text{O}_2$ and 1:2:2:1 quartet signal of $\cdot\text{OH}$

665 confirmed the generation of $^1\text{O}_2$ and $\cdot\text{OH}$, with signal intensities increasing as the

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666 reaction time progressed (Fig. S10). It should be noted that EPR-based spin-trapping
667 methods have inherent limitations. For example, spectral overlap and background
668 signals may affect the resolution and accuracy of peak assignment. Furthermore,
669 certain short-lived or low-reactivity ROS may not be effectively captured by the
670 selected spin traps. Therefore, the reported ROS contributions should be interpreted as
671 semi-quantitative estimates rather than absolute concentrations

删除[bess_yc]: (Fig. S10). Moreover

672 Then, a chemical probe method was employed to further quantify the
673 concentrations of $\cdot\text{OH}$ and $^1\text{O}_2$. Benzoic acid (BA) was used as the $\cdot\text{OH}$ probe
674 compound according to previously established protocol (Hu et al., 2025). Briefly, six
675 different concentration of BA (5, 10, 15, 20, 30, 40 and 50 μM) were added to
676 separate aliquots of the same extract. After illuminating for time t , the residual BA
677 concentration was monitored by UPLC-PDA. A linear regression of $-\ln[\text{BA}]/\ln[\text{BA}]_0$
678 versus reaction time t yielded the pseudo-first-order rate constant (k_{BA}) (Fig. 10 a, b).
679 By plotting the reciprocal ($1/k_{\text{BA}}$) against $[\text{BA}]$, the intercept was obtained (Fig. 10 c),
680 from which $[\text{OH}]_{\text{ss}}$, was determined by dividing the intercept by the second-order rate
681 constants $k_{\text{BA}, \text{OH}}$ (Lei et al., 2023). The $k_{\text{BA}, \text{OH}}$ is strongly dependent on pH value.

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682 Under low pH conditions, benzoic acid predominantly exists in its molecular form
683 (BA), whereas at high pH it is mainly present as the deprotonated species (benzoate,
684 BA^-). These different forms exhibit distinct reactivity toward $\cdot\text{OH}$. According to the
685 literature (Arakaki et al., 2013), when $\text{pH} > 6$, BA^- is the dominant species, with a
686 rate constant $k_{\text{BA}^-, \text{OH}} = 6.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; when $\text{pH} < 4$, the molecular form dominates,
687 with $k_{\text{BAOH}} = 1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. In this study, the initial pH values of coal and maize
688 samples were 6.79 and 5.83, therefore, $5.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Lei et al., 2023) was
689 adopted to calculate the steady-state concentration of $\text{OH}\cdot$. The estimated $[\text{OH}]_{\text{ss}}$ were

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690 9.11×10^{-14} M and 8.58×10^{-14} M for coal and maize smoke extracts, respectively (Fig.
691 10)—values comparable to those typically observed in atmospheric cloud droplets
692 (Arakaki et al., 2013; Li et al., 2023).

693 The steady-state concentrations of $^1\text{O}_2$ and $^3\text{C}^*$ were also quantified by
694 monitoring the decay of furfuryl alcohol (FFA) and syringol (SYR) under
695 pseudo-first-order kinetics (Fig. 10 d-f), following previously established procedures

696 (Li et al., 2024). Considering the relatively high $\bullet\text{OH}$ concentration in the mixed
697 system, potential interference may occur when using FFA as a probe, since it can react
698 with both $\bullet\text{OH}$ ($k_{\text{FFA}, \text{OH}} = 1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) and $^1\text{O}_2$ ($k_{\text{FFA}, ^1\text{O}_2} = 1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). To
699 eliminate this interference, excess methanol was added to completely quench $\bullet\text{OH}$
700 ($k_{\text{MeOH}, \text{OH}} = 1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) before employing FFA to determine the $^1\text{O}_2$ concentration.

701 The results (Fig. 10) showed that the $[^1\text{O}_2]_{\text{ss}}$ values were 3.48×10^{-13} M and 1.8×10^{-12}
702 M for coal and maize smoke extracts, respectively, higher than that reported for 5
703 mgC L⁻¹ of SOA extracts (3×10^{-14} M) (Manfrin et al., 2019). Generally, $^1\text{O}_2$ was born

704 by triplets thus tightly linked to $^3\text{C}^*$. The significantly higher $^1\text{O}_2$ concentration
705 observed in maize smoke extracts—approximately six times that of coal smoke
706 extracts—indicates a greater abundance of triplet-state precursors in maize-derived
707 WSOM. Similarly, SYR was employed as a chemical probe due to its high reactivity
708 with triplets ($k_{\text{SYR}, ^3\text{C}^*} = 3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (Ma et al., 2023). Based on its
709 pseudo-first-order decay kinetics, the steady-state concentrations of $^3\text{C}^*$ in the maize
710 and coal systems were determined to be 9.0×10^{-13} M and 7.05×10^{-13} M, respectively
711 (Fig. 11f).

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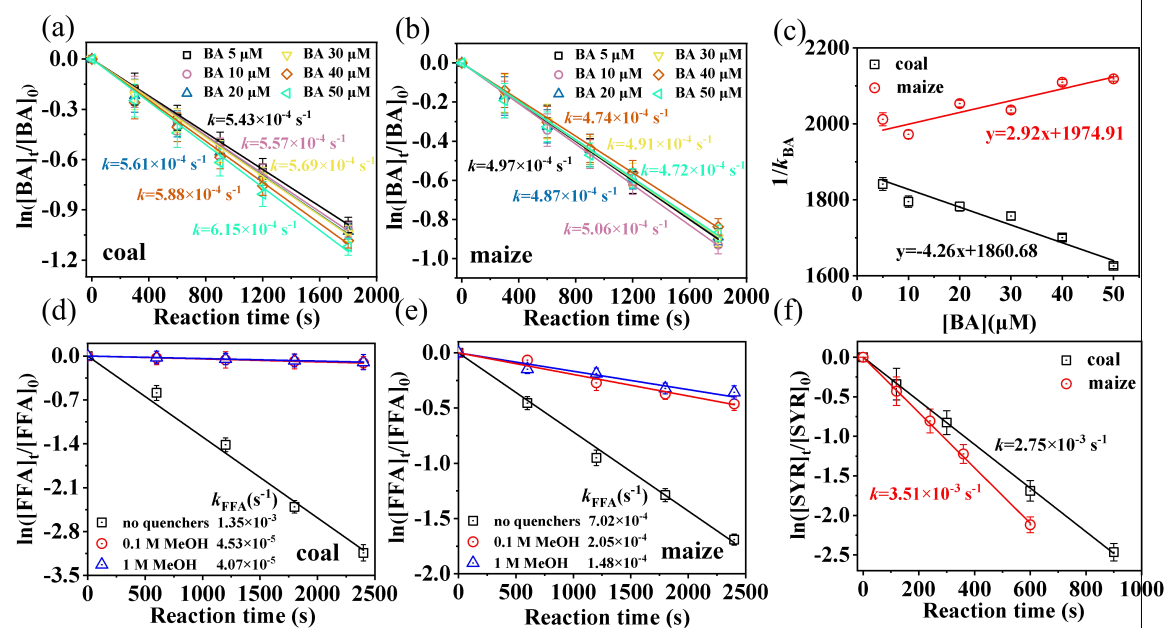
712 The steady-state concentrations determined in our system are approximately one
713 order of magnitude higher than those reported in aqueous PM extracts illuminated
714 with 365 nm lamps (e.g., $\sim 10^{-13}$ M for triplets) (Bogler et al., 2022). Data from Ma et
715 al. (2024) also showed the concentrations of $\bullet\text{OH}$, $^1\text{O}_2$, and $^3\text{C}^*$ in $\text{PM}_{2.5}$ extracts range
716 from $(0.2\text{--}4.7) \times 10^{-15}$ M, $(0.7\text{--}45) \times 10^{-13}$ M, and $(0.03\text{--}7.9) \times 10^{-13}$ M, respectively.
717 This significant difference is mainly attributed to the addition of 10 mM H_2O_2 in our
718 experiments. Given an estimated average molecular weight of 300 g/mol for WSOM,
719 the resulting molar ratio of H_2O_2 to WSOM (15 mg C/L) is approximately 200:1. This
720 substantial excess of H_2O_2 provides a high concentration of $\bullet\text{OH}$, sufficient to
721 extensively oxidize WSOM and explaining why our $\bullet\text{OH}$ levels are orders of
722 magnitude greater than those in typical PM extracts (Ma et al., 2024).

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723 Consequently, the degradation of WSOM in our system is predominantly driven
724 by $\bullet\text{OH}$ oxidation, with minor contributions from other reactive species. Furthermore,
725 the concentrations of $^1\text{O}_2$ and $^3\text{C}^*$ were also slightly higher than those in ambient PM
726 extracts (Ma et al., 2024), likely because our simulated combustion samples contained
727 higher levels of phenolic compounds and PAHs, which are known precursors for these
728 species.

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729

730 **Fig. 10.** Loss of (a,b) BA, (d,e) FFA, (f) SYR and (c) plot of $1/k_{BA}$ and BA concentration

731 To elucidate the reaction mechanism, the role of different ROS in the photodecay

732 and light absorbance of smoke extracts were examined. The absorption spectra of

733 smoke extracts with and without 0.1 M methanol (CH_3OH quencher) were compared

734 (Fig. S11). A molar ratio of 2000:1(MeOH: WSOM) was employed, assuming an

735 average molecular weight of 300 g/mol, to ensure complete scavenging OH given the

736 comparable second-order rate constants of MeOH and WSOM with OH (Liu-Kang

737 et al., 2024). As shown in Fig. S11, absorbance decay rate decreased markedly,

738 especially within the first hour, indicating that OH play a dominant role in the

739 photodecay of the extracts.

740 To further assess the contributions of individual ROS, comparative experiments

741 were conducted under N_2 -, air-, and O_2 -saturated conditions. Under N_2 saturation,

742 secondary oxidants such as $\text{HO}_2\cdot$ and $\cdot\text{OH}$ were largely excluded due to the absence

743 of oxygen. The changes in WSOC indicate that direct photolysis in both smoke

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744 extracts was much weaker than $\bullet\text{OH}$ oxidation. Under $\bullet\text{OH}$ oxidation, the WSOC
745 loss under N_2 -saturated conditions was much lower than that under O_2 - and
746 air-saturated conditions (Fig. S12), whereas in direct photolysis, the differences
747 among the three gas conditions were negligible (Fig. S13). This suggests that O_2 plays
748 a crucial role only for $\bullet\text{OH}$ oxidation.

749 Previous studies have reported that $^3\text{C}^*$ -initiated photooxidation of phenolic
750 compounds proceeds most rapidly under N_2 -saturated conditions (Lei et al., 2023). In
751 contrast, our results showed the fastest degradation under O_2 -saturated and the slowest
752 under N_2 , implying that $^3\text{C}^*$ is not the dominant oxidant in our system. This
753 conclusion is further supported by the comparable WSOC degradation observed for
754 coal and maize smoke extracts. Theoretically, if $^3\text{C}^*$ were the primary oxidant, maize
755 extracts would be expected to exhibit a much higher WSOC degradation owing to
756 their greater content of photosensitizers, as indicated by the higher lignin-like
757 compounds in maize (Section 3.3).

758 The relative importance of individual ROS in WSOM photodecay was evaluated
759 by multiplying their corresponding second-order rate constants with their steady-state
760 concentrations. Thus, we estimated the relative role in smoke WSOM photodecay.
761 Given that reaction rates of WSOC with αOH and $^3\text{C}^*$ were $3.8 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ and
762 $7.2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$, whereas $^1\text{O}_2$ reacts much more slowly ($10^5 \text{ M}^{-1}\text{s}^{-1}$) (Ma et al., 2024),
763 the contributions were calculated (Fig. 10b). For coal smoke extract, αOH , $^3\text{C}^*$, $^1\text{O}_2$
764 accounted for approximate 86.4%, 12.8% and 0.8% of the total oxidation, respectively.
765 A similar pattern was observed for maize smoke extracts (80.9%, 16.0% and 3.1%),

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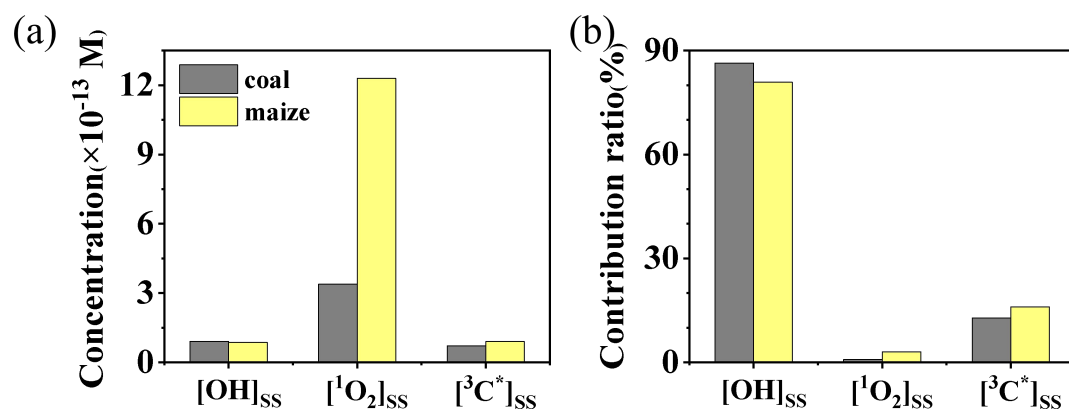
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766 with the overall contribution order of $\bullet\text{OH} > {}^3\text{C}^* > {}^1\text{O}_2$. Although ${}^1\text{O}_2$ exhibited the
 767 highest steady-state concentration, its low reactivity limited its overall contribution,
 768 consistent with previous findings (Zhang et al., 2024). According to earlier reports
 769 (Tang et al., 2025), when the concentration of the BB-derived mixture reaches 12 mg
 770 C/L, the concentration of photosensitizers in solution can exceed several millimoles.
 771 Therefore, ${}^3\text{C}^*$ also plays an important and non-negligible role in the
 772 photodegradation of both smoke WSOM.



773

774 Fig. 11. ROS steady-state contribution and their contribution to WSOM photodecay

775 Surely, different H_2O_2 concentrations might influence the relative role of ROS. To
 776 assess this effect, we examined the ROS concentrations and their contributions under
 777 five different H_2O_2 levels (0.5, 1, 3, 5, and 10 mM). The results are presented in Table
 778 S5. As shown in Table S5, increasing the H_2O_2 dosage leads to higher $\bullet\text{OH}$
 779 concentrations and relative contributions, accompanied by a corresponding decrease
 780 in the contribution of triplet excited states (${}^3\text{C}^*$). The measured $\bullet\text{OH}$ concentrations
 781 generally fall within a relatively narrow range under five different H_2O_2 concentration,
 782 with average values of $(0.7 - 9.1) \times 10^{-14} \text{ M}$ and $(1.3 - 8.3) \times 10^{-14} \text{ M}$, for coal and maize
 783 smoke WSOM, respectively. Specifically, we also noted that the ${}^1\text{O}_2$ contribution is

784 only weakly affected by the H₂O₂ concentration. Given that this study mainly focuses
785 on the role of •OH, all subsequent experiments were conducted at a relatively high
786 H₂O₂ concentration. While additional experiments at varying H₂O₂ concentrations
787 would provide valuable quantitative constraints on these processes, they are beyond
788 the scope of the present study.

789 **3.6.2 Photochemical transformation of smoke extracts**

790 By introducing extra H₂O₂, the •OH concentration and its role in the photoaging
791 of both smoke extracts were altered. The added •OH accounts for a major fraction of
792 the total oxidants in both systems, thereby influencing the overall optical properties
793 and chemical composition. Based on the ROS measurements and molecular analyses,
794 a conceptual mechanism for the aqueous photooxidation of both smoke extracts is
795 proposed (Fig. 12). Upon irradiation, photosensitizers in WSOM absorb photons and
796 form triplet excited states (³PS*), which transfer energy or electrons to dissolved O₂,
797 generating various ROS (¹O₂, O₂⁻, •HO₂, and •OH). These reactive species initiate and
798 propagate oxidation processes, thereby modifying the chemical composition and
799 optical properties of WSOM.

800 In the first stage, abundant •OH rapidly attacks electron-rich aromatic and
801 conjugated structures, cleaving C=C and C–O bonds and causing a sharp decrease in
802 WSOC and light absorbance. Meanwhile, both ³Sen* and ¹O₂ selectively oxidizes
803 lignin-like compounds, forming oxygenated intermediates such as carbonyls, and
804 carboxylic acids, resulting in gradual decrease in solution pH (Fig. S7) and increase in
805 O/C.

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806 As the reaction proceeds, the depletion of aromatic chromophores suppresses
807 further ROS formation, consistent with the observed decline in DTT activity. FT-ICR
808 MS analysis further supports this evolution, revealing a shift from high H/C, low O/C
809 aromatic compounds toward lipid- or aliphatic-like species.

810 Interestingly, although total WSOC decreased with aging, WSOC-normalized
811 DTT activity increased due to probable highly DTT active species (e.g., quinone-like
812 species). Similar trends have been observed in BBOA-WSOC OH-photooxidation
813 aging, where oxidative potential decreased at the initial period (~ 5 h) despite WSOC
814 mass loss (Wong et al., 2019).

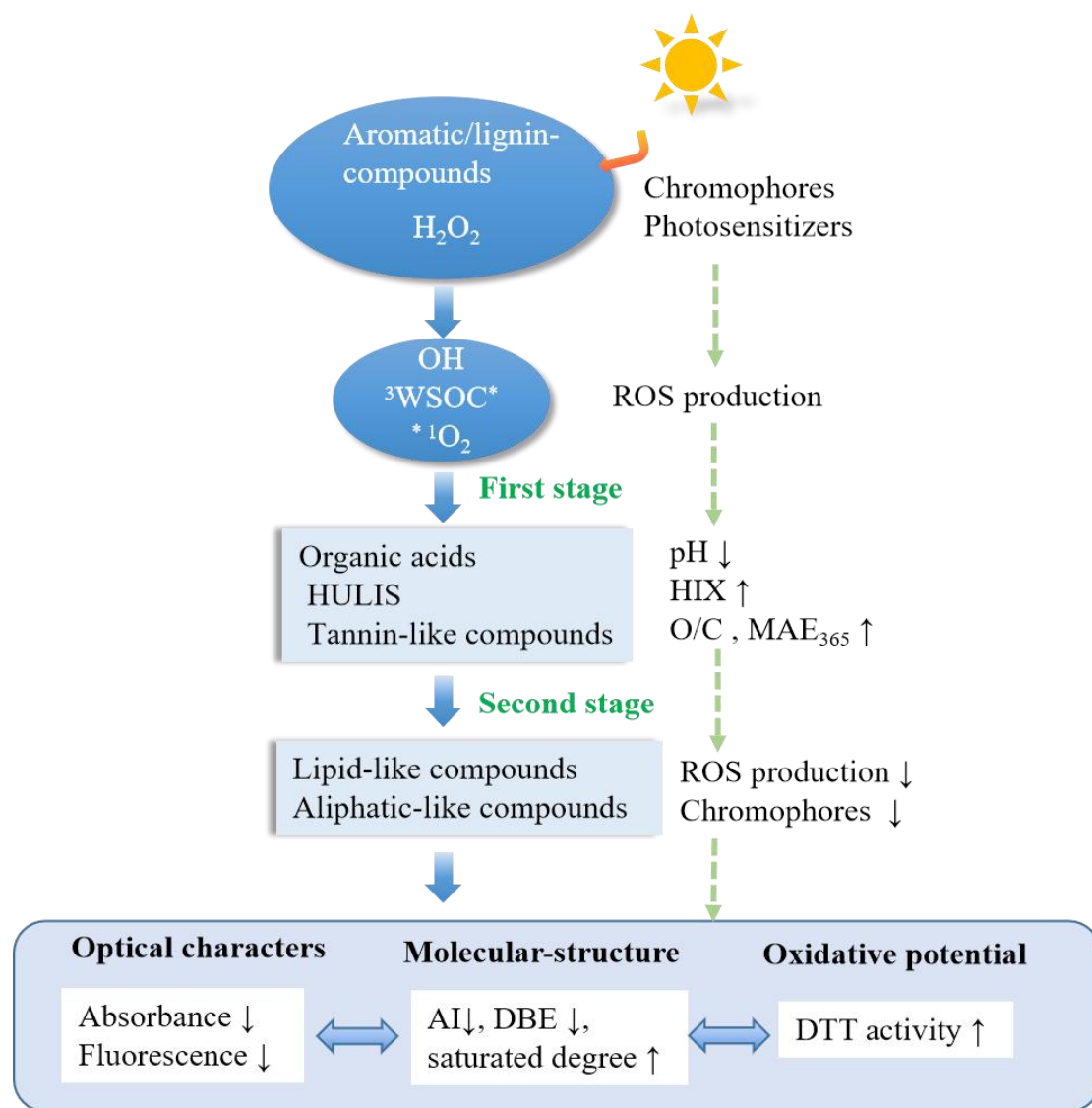
815 Overall, the aqueous photooxidation of two smoke extracts involves a dynamic
816 interplay among $\bullet\text{OH}$, $^3\text{C}^*$, and $^1\text{O}_2$. The early stage is dominated by $\bullet\text{OH}$ -driven
817 degradation of chromophores, followed by secondary formation of oxygenated,
818 potentially more toxic species through $^1\text{O}_2$ and triplet-state reactions. These processes
819 jointly govern the chemical evolution, light-absorbing behavior, and oxidative
820 potential of WSOM during photochemical aging.

| 删除[bess_je]: combustion-emitted

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| 删除[bess_je]: $^1\text{O}_2$.

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821

822 **Fig. 12.** Proposed photochemical transformation pathways for two smoke extracts

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823 Next, by integrating FT-ICR MS and ROS analyses, we further compared the
 824 molecular transformation mechanisms of the two types of smoke. Table S6 and S7 list
 825 the top 10 most abundant compounds identified by FT-ICR MS before photolysis and
 826 after 11 h and 23 h of irradiation, together with their DBE values, molecular formulas,
 827 inferred functional groups, and FT-ICR MS classifications.

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828 Fresh coal-derived WSOM is mainly composed of CHO and CHOS compounds,
 829 including organosulfates (e.g., C₁₂H₂₆O₄S, C₁₇H₂₈O₃S, and C₁₈H₃₀O₃S), aromatic
 830 oxygenated species (e.g., C₁₂H₁₂O₅ and C₁₃H₁₄O₅), and aliphatic compounds (e.g.,
 831 C₁₈H₃₆O₃). During photochemical processing, only limited transformation is observed

832 among the top 10 compounds, although partial conversion of lignin-like structures
833 into lipid-like species occurs. Several molecular formulas (e.g., C₁₇H₂₈O₃S,
834 C₁₈H₃₀O₃S, C₁₆H₃₂O₂, and C₁₈H₃₆O₃) persist before and after 11 h of irradiation,
835 indicating their relative resistance to photochemical degradation. Consequently, the
836 average molecular weight of coal-derived WSOM exhibits only minor variation
837 during oxidation.

838 The transformation of coal smoke WSOM can be summarized by three main
839 pathways. First, aromatic compounds (e.g., C₁₂H₁₂O₅ and C₁₃H₁₄O₅)
840 undergo •OH-driven oxidation and tend to break down into smaller molecules,
841 contributing to the loss of aromatic structures. Second, aliphatic compounds (e.g.,
842 C₁₈H₃₆O₃) are oxidized via •OH-initiated functionalization, forming more stable
843 oxygenated fatty acid-like products such as C₁₆H₃₂O₂ and C₁₈H₃₆O₂, along with
844 partially oxidized intermediates (e.g., C₁₈H₃₄O₃). Third, CHOS compounds exhibit
845 partial stability, with long-chain organosulfates (e.g., C₁₈H₃₀O₃S) persisting
846 throughout the oxidation process.

847 In contrast, maize smoke WSOM shows distinctly different behavior. The fresh
848 sample was dominated by lignin-like compounds, such as C₉H₁₀O₃ and C₉H₈O₃,
849 reflecting the prevalence of aromatic structures derived from biomass combustion.
850 During aqueous-phase oxidation, these compounds undergo extensive transformation
851 driven primarily by •OH attack, including hydrogen abstraction and electrophilic
852 addition to aromatic rings. These reactions promote hydroxylation, denitration, and
853 subsequent ring-opening processes, leading to the formation of highly oxygenated and
854 lower-molecular-weight products. As a result, both aromaticity and average molecular
855 weight decrease significantly. This trend is supported by the appearance of highly
856 oxygenated species (e.g., C₉H₁₀O₇ and C₉H₁₈O₆ at 11 h), which shift toward higher

857 O/C ratios in the Van Krevelen space. Meanwhile, lignin-like compounds are
858 progressively transformed into lipid-like, tannin-like, and aliphatic species. Notably,
859 the top 10 products at 11 h and 23 h exhibit strong similarity (e.g., C₁₄H₂₂O, C₁₆H₃₂O₂,
860 C₁₈H₃₆O₂, and C₁₂H₂₆O₄S), suggesting the formation of relatively stable oxidation
861 products at later stages.

862 Overall, these results demonstrate that maize smoke undergoes more extensive
863 oxidation, characterized by pronounced aromatic degradation and molecular
864 fragmentation, whereas coal smoke exhibits higher chemical stability, with limited
865 molecular transformation and a greater persistence of initial compounds.

866 **4 Conclusions**

867 This study systematically investigated the aqueous-phase •OH-driven
868 photodegradation of coal and maize smoke extracts, providing molecular-level
869 insights into their molecular and optical evolution. EEM-PARAFAC resolved one
870 humic-like and two protein-like components, revealing distinct temporal patterns
871 between coal and maize systems. FT-ICR MS further showed that both samples were
872 dominated by CHO and CHON compounds, with maize smoke enriched in CHON
873 species and coal smoke containing a higher fraction of sulfur-containing compounds.

874 Aqueous photooxidation led to increased molecular saturation and reduced
875 aromaticity, as evidenced by declining DBE and AI values. Lignin-like compounds
876 were progressively depleted, accompanied by an increase in lipid- and aliphatic-like
877 species, suggesting the breakdown of conjugated structures and the formation of more
878 saturated, oxygenated products. These transformations reduced chromophoric content
879 through double-bond cleavage and aromatic ring opening, resulting in decreased light
880 absorption and fluorescence.

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881 The contributions of ROS to photodegradation followed the order $\bullet\text{OH} > {}^3\text{C}^* >$
882 ${}^1\text{O}_2$, highlighting the dominant role of $\bullet\text{OH}$ in aqueous-phase processing. Despite
883 these common trends, distinct photochemical pathways were observed. Maize-derived
884 WSOM exhibited more rapid oxidation during the early stage, likely driven by
885 OH-functionalization reactions, whereas coal-derived WSOM showed greater
886 compositional stability. Mechanistically, ROS promoted the conversion of lignin-like
887 aromatics into highly oxygenated products via hydroxylation and ring-opening, while
888 lipid-like compounds undergo functionalization and fragmentation. Secondary
889 reactions with sulfate lead to the formation of organosulfates.

890 HR-AMS results confirmed the formation of low-molecular-weight carboxylic
891 acids (e.g., oxalate), accompanied by decreasing pH and increasing oxidation state of
892 aqSOA, particularly in maize systems. Although total WSOC decreased during
893 photodegradation, the WSOC-normalized oxidative potential increased, as indicated
894 by enhanced DTT consumption, likely due to the formation of nitrogen-containing
895 compounds in coal smoke and reactive quinones in maize smoke. Furthermore,
896 maize-derived aqSOA exhibited higher oxidation levels, whereas coal smoke
897 produced higher aqSOA mass yields.

898 Overall, aqueous-phase photochemical processing simultaneously weakens
899 optical properties and enhances chemical reactivity. From an atmospheric perspective,
900 cloud and fog processing can substantially modify the properties of smoke-derived
901 WSOM. The transformation of aromatic chromophores into more saturated products
902 reduces brown carbon light absorption, potentially weakening its direct radiative
903 forcing. At the same time, the formation of highly oxidized and redox-active species
904 may enhance aerosol oxidative potential and toxicity. These findings underscore the

删除[bess_je]: Distinct photodegradation pathways were observed for coal and maize extracts.

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删除[bess_je]: fluorescence while enhancing oxidative potential. Maize smoke aqSOA exhibited higher oxidation degrees than coal, whereas coal smoke generated a higher aqSOA mass yield. The observed molecular evolution and photochemical

删除[bess_je]: indicate that water-soluble products from biomass and coal combustion undergo distinct pathways during

删除[bess_je]: aging.

These findings suggest that aqueous-phase photochemistry

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删除[bess_je]: of biomass and coal emissions.

Simultaneously

删除[bess_je]: products, including quinones

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905 importance of incorporating aqueous-phase transformations into atmospheric models
906 to more accurately assess the climate and air quality impacts of emissions from
907 different fuel sources.

删除[bess_je]: toxicity of aged aerosols, influencing cloud chemistry, secondary organic aerosol formation, and heterogeneous reactions in the atmosphere. Incorporating these

删除[bess_je]: is therefore essential

删除[bess_je]: smoke

908 **Author contributions.**

909 ZY and XG developed the research objectives and designed the experiments. DH
910 and XH set up the combustion sampling apparatus and collected samples. DH and QC
911 conducted the photochemistry experiments and analyzed the data with the help of XH.
912 ZY prepared the manuscript with contributions from all co-authors. ZY and XG
913 provided supervision and guidance during the experiments and writing.

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916 Jiangsu Province (BK20221405) and National foreign expert project (H20240368).
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920 Innovation Program of Jiangsu Province (SJCX24_1808).

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