https://doi.org/10.5194/acp-2019-608
Preprint. Discussion started: 14 October 2019

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Molecular Composition and Photochemical Evolution of Water Soluble Organic Carbon (WSOC) Extracted from Field Biomass Burning Aerosols using High Resolution Mass Spectrometry

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https://doi.org/10.5194/acp-2019-608
Preprint. Discussion started: 14 October 2019

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ABSTRACT

Photochemistry plays an important role in the evolution of atmospheric water soluble organic carbon (WSOC), which dissolves into clouds, fogs and aerosol liquid water. In this study, we examined the molecular composition and evolution of a WSOC mixture extracted from fresh biomass burning aerosols upon photolysis, using direct infusion electrospray ionization high-resolution mass spectrometry (ESI-HRMS) and liquid chromatography coupled with mass spectrometry (LC/ESI-HRMS). For comparison, two typical phenolic compounds (i.e., phenol and guaiacol) emitted from lignin pyrolysis in combination with hydrogen peroxide (H_2O_2) as a typical OH radical precursor, were exposed to simulated sunlight irradiation. The photochemistry of both, the phenols (photo-oxidation) and WSOC mixture (direct photolysis) can produce a series of highly oxygenated compounds which in turn increases the degree of oxidation of organic composition and acidity of the bulk solution. In particular, the LC/ESI-HRMS technique revealed significant photochemical evolution on the WSOC composition, e.g., the photodegradation of low oxygenated species and the formation of highly oxygenated products. We also tentatively compared the mass spectra of photolytic time-profile extract with each other for a more comprehensive description of the photolytic evolution. The calculated average oxygen-to-carbon (O/C) ratios of oxygenated compounds in bulk extract increases from 0.38±0.02 to 0.44±0.02 (mean±standard deviation) while the intensity (S/N)-weighted average O/C (O/C_w) increases from 0.45±0.03 to 0.53 ±0.06 as the time of irradiation extends from 0 to 12h. These findings indicate that

https://doi.org/10.5194/acp-2019-608
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the water soluble organic fraction of fresh combustion-derived aerosols have the potential to form more oxidized organic matter, accounting for the highly oxygenated nature of atmospheric organic aerosols.

1 INTRODUCTION

Water-soluble organic carbon (WSOC) comprises a significant fraction of atmospheric aerosols, accounting for 20–80% of total organic carbon (OC) (Krivacsy et al., 2001; Wozniak et al., 2008; Fu et al., 2015; Xie et al., 2016).WSOC is directly involved in the formation of cloud condensation nuclei (CCN) by modifying the aqueous chemistry and surface tension of cloud droplets (Graham et al., 2002; Nguyen et al., 2012; Zhao et al., 2013; McNeill 2015). Despite its significance, little is known about the chemical composition and sources of WSOC, with less than 10–20% of the organic mass being structurally identified (Cappiello et al., 2003; Fu et al., 2015). Biomass burning is a well-known emission source of WSOC (Anastasio et al., 1997; Fine et al., 2001; Graham et al., 2002; Mayol-Bracero et al., 2002; Gilardoni et al., 2016).Although the composition varies with fuel type and combustion conditions (Simoneit 2002; Smith et al., 2009), the WSOC mixture often covers a common range of polar and oxygenated aromatic compounds (Graham et al., 2002; Mayol-Bracero et al., 2002; Duarte et al., 2007; Chang and Thompson 2010; Yee et al., 2013; Gilardoni et al., 2016) with molecules incorporating different numbers of functional groups like COOH, C=O, CHO, COH, COC, $CONO_2$, CNH, and/or $CONH_2$ groups (Graham et al., 2002). In particular, lignin pyrolysis often yields a large amount of aromatic alcohols, carbonyl, and acid compounds

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(Mayol-Bracero et al., 2002; Chang and Thompson 2010; Gilardoni et al., 2016). Once dissolved into cloud, fog, and even aerosol liquid water, these substances can undergo aqueous-phase reactions to affect aerosol evolution processes under sunlight irradiation, and produce low-volatility species, which have the potential to form secondary organic aerosol (SOA) after water evaporation (Graham et al., 2002; Cappiello et al., 2003; Duarte et al., 2007; Sun et al., 2010; Yu et al., 2014).

Field and laboratory studies have demonstrated that aqueous photochemical processes contribute significantly to the aqueous SOA formation from biomass burning precursors and the evolution of smoke particles (Sun et al., 2010; Lee et al., 2011; Kitanovski et al., 2014; Yu et al., 2014; McNeill 2015; Gilardoni et al., 2016). Gilardoni et al. (2016) observed aqueous SOA formation in both fog water and wet aerosols, resulting in an enhancement in the oxidized OA, and following atmospheric aging the overall O/C ratios of aerosols has also increased. In laboratory studies, phenols and methoxyphenols (important biomass burning emerged intermediates) are often used as SOA precursors to examine the photochemical evolution in aqueous environment and aerosol-forming potential under relevant atmospheric conditions (Chang and Thompson 2010; Sun et al., 2010; Smith et al., 2014; Yu et al., 2014, Vione et al., 2019). The corresponding photochemical products formed through hydroxylation, oligomerization, and fragmentation typically cover a series of low-volatility and highly oxygenated species. For instance, the methoxyphenol-derived SOA are proposed as a proxy for atmospheric humic-like substances (HULIS) (Ofner et al., 2011; Yee et al., 2013). Other compounds emitted

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from lignin pyrolysis, e.g., aromatic alcohol, carbonyl, and carboxylic species retaining the phenyl ring have also been found to produce colored products via aqueous photo-oxidation, which may become a part of HULIS (Chang and Thompson 2010, Huang et al., 2018). In addition, photochemical processing of common water-soluble aliphatic compounds such as aldehydes (Lim and Turpin 2015), polyols (Daumit et al., 2014), and organic acids (Griffith et al., 2013) in aqueous solution can also lead to the formation of oligomers, highly oxygenated and multifunctional organic matter (McNeill 2015).

In recent years, high resolution mass spectrometry (HRMS) has been commonly applied to study the organic molecular composition in cloudwater (Zhao et al., 2013; Boone et al., 2015), fogwater (Cappiello et al., 2003), rainwater (Altieri et al., 2009a; Altieri et al., 2009b), laboratory-generated SOA (Bateman et al., 2011; Romonosky et al., 2015; Lavi et al., 2017), and field-collected aerosol samples (Laskin et al., 2009; Lin et al., 2012a; Lin et al., 2012b; Kourtchev et al., 2013). It has also been used in time-profile observations of the photochemical evolution of aqueous extracts from laboratory-generated SOAs (Bateman et al., 2011; Romonosky et al., 2015). However, direct infusion MS methods are prone to ion suppression caused by other organic species, inorganic salts, and adduct formation (Kourtchev et al., 2013). Therefore, HRMS coupled with LC might be another complementary powerful tool for relieving ion suppression (Kourtchev et al., 2013; Wang et al., 2016). It could also provide more information enabling the identification of possible isomers from the ions with same mass-to-charge ratio (m/z).

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To our knowledge, the aqueous photochemical evolution of WSOC extracted from real ambient aerosols has not been studied in detail at the molecular level. The present study is focused on a further analysis of the previously studied field collected samples by Cai et al. (2018). Here, the main goal is to investigate the molecular characteristics of water-soluble organic molecules by the photochemical evolution using ESI-HRMS and LC/ESI-HRMS performed in negative ionization mode. The photochemistry of phenol and guaiacol was evaluated under laboratory conditions as well, and used as a reference.

2 EXPERIMENTAL SECTION

2.1 Particulate sample collection and preparation of aqueous extracts

Fresh straw-burning aerosols were collected during the summer harvest season of 2013, at rural fields in north China (Cai et al., 2018). Briefly, the selected samples used for HRMS analysis were collected from two sampling sites, located at rural fields in Wenxian in Henan Province (noted: HNWX) and Daming county in Hebei Province (HBDM). The selected sampling sites were mainly affected by heavy smog from straw burning (Figure 1). As described in Cai et al. (2018), particulate matter ($\leqslant$2.5μm) was sampled by a portable particulate sampler (MiniVol TAS, AirMetrics, USA), with quartz filters (47mmin diameter, QMA, Whatman, UK) baked at 600°C for 6 hours before sampling.

The preparation of straw-burning particle extracts and measurements for carbon content including organic carbon (OC), elemental carbon (EC) and WSOC were

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described in detail in Cai et al. (2018). A pH meter (Mettler Toledo SevenEasy^{TM} S20) calibrated at pH 4.00 and 6.86 was applied for extract pH measurements. Prior to analysis the extract solutions were stored at -20°C in the dark. To reduce the WSOC mass loss, the desalting treatment (e.g., solid phase extraction (SPE)) was not performed on these samples.

Figure 1. One field site at Daming, Hebei province, China, for sampling the aerosols affected by biomass burning.

2.2 Laboratory observation of the direct photolysis of WSOC extracts

A 12-hour direct photolysis of particle extracts was performed in a photoreactor (BL-GHX-V, Bilon Instruments Co. Ltd., China, see Figure S1) (Cai et al., 2018). In the wavelength range of 310-400 nm relevant to the boundary layer of the atmosphere, the actinic flux of the lamp is about 5 times stronger than the solar actinic flux, meaning that the spectral evolution via the 12-hour simulated solar irradiation might be equal with the effect caused by actual sunlight irradiation with a

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duration of at least 60 hours. As described in Cai et al. (2018), the water extraction resulted in a dilution of the collected organic compounds, however, the ratio of the water mass to $PM_{2.5}$ mass for extraction was compatible with the ratio of water mass to WSOC content in cloud water, indicating that the present aqueous extracts are relevant to the atmospheric cloud water condition (Li et al., 2017).

In the experimental section of phenol photochemistry, initial solution of 0.1 mM phenol and 0.1 mM guaiacol in combination with an OH radical precursor (0.1 mM H_2O_2), were prepared in ultra-pure water (Milli-Q, Milipore). The pH of the solution was adjusted to 5 with 0.1 M sulfuric acid (H_2SO_4), which is usually relevant to the acidity in fog and cloud waters (Collet et al., 1998, Fahey et al., 2005). The prepared solution and reference blank were irradiated by simulated sunlight irradiation with a duration of 4 hours. Hereby, we mainly focus on acquiring the chemical characteristics of aqueous products of phenols, and tentatively identify some biomarkers (e.g., phenolic dimers) whether they exist in the real biomass burning particulate samples.

2.3 Sample analysis

The direct infusion MS analysis was conducted using a Thermo Scientific Orbitrap Fusion Tribrid mass spectrometer equipped with a quadrupole, orbitrap, and linear ion trap mass analyzers, with a heated ESI source. To assist in ionization and desolvation, the aqueous extract was diluted to a 1:1 mixture of acetonitrile and sample by volume. The full scan mass spectra were acquired in negative ionization mode, with a resolution of 120 000 at *m/z* 200 for the orbitrap analyzer and a mass

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scan range of m/z 50-750. Before determination, the orbitrap analyzer was externally calibrated for mass accuracy using Thermo Scientific Pierce LTQ Velos ESI calibration solution. The direct infusion parameters were as follows: sample flow rate 5μl min^{-1}; capillary temperature 300°C; S-lens RF 65%; spray voltage -3.5kV; sheath gas, auxiliary gas, and sweep gas flows were 10, 3, and 0 arbitrary units, respectively. Data collecting was performed when the intensity of the total ion current (TIC) maintained constant with an RSD＜5%. At least 100 data points (mass spectral scans) were collected for each test sample, and the each exported mass spectra for analysis was derived from the average result of 100 spectrums.

The LC/ESI-HRMS analysis operated in negative ionization mode was performed using a U3000 system coupled with a T3 Atlantis C18 column (3μm; 2.1×150mm; Waters, Milford, USA) and an Orbitrap Fusion MS. A 10 μL extract was injected, with a flow rate of 0.2 ml min^{-1} for the mobile phase, which consisted of H_2O (A) and acetonitrile (B). The gradient applied was 0-5 min 3% B; 5-20 min from 3 to 95% (linear), and kept for 25 min at 95%; and 45-50 min from 95 to 3%, and held for 10 min at 3% (total run time 60 min).

2.4 Data processing

Mass spectral peaks with three times larger than the signal to noise ratio (S/N) were extracted from the raw files. Peaks in both sample and blank spectra were retained if their intensity in the former was five times larger than in the latter. A molecular assignment based on the accurate mass was performed using Xcalibur software (V3.0 Thermo Scientific) with the following constraints: $^{12}C \leq 50$, $^{13}C \leq 1$,

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$^{1}H \leq 100$, $^{16}O \leq 50$, $^{14}N \leq 4$, $^{32}S \leq 1$, and $^{34}S \leq 1$. All mathematically possible elemental formulas, with a mass tolerance of ±3ppm were calculated. Elemental formulas containing ^{13}C or ^{34}S were checked for the presence of ^{12}C or ^{32}S counterparts, respectively. If they were not matched with the corresponding monoisotopic formulas, then the assignment with next larger mass error was considered. Isotopic and unassigned peaks were excluded from further analysis.

Ions were also characterized by the number of rings plus double bonds (i.e., double bond equivalents (DBE)), which were calculated as: DBE=c-h/2+n/2+1 for an elemental composition of $C_cH_hO_oN_nS_s$. The assigned formula was additionally checked with the nitro-rule. For ambient samples, based on the presence of various elements in a molecule, the identified elemental formulas were classified into several main compound classes: CHO (i.e., molecules containing only C, H, and O atoms), CHOS, CHON, and CHONS, and others including CHN and CHS. In the present study, because the detected water-soluble ions almost were below m/z 400, we focused our molecular analysis on m/z 50-400.

3 RESULTS AND DISCUSSION

3.1 Mass spectral characteristics of WSOC in biomass burning particulate

The PM2.5 concentration in present straw burning smoke samples ranges from 6.46 to 28.03 mg m^{-3} (Table S1). OC is the major component of the collected PM2.5 with a proportion of 50.9 ± 7.6% (mean ± standard deviation), whereas EC represents a negligible fraction (average 1.3±0.4%). Meanwhile, WSOC accounts for 35.5±7.5% of OC in the tested samples.

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Four extract samples (HNWX-1, HNWX-2, HBDM-1 and HBDM-2) (Table S1) analyzed using high resolution mass spectrometry showed similar patterns in mass distribution of water-soluble molecular species that mainly range from 50 to 400 Da. A group of reconstructed mass spectrum (abstracted blank) for two representative samples HNWX-1, and HBDM-1 is shown, as an example, in Figure 2. In mass range 50-400 Da, there were 827±44 molecular formulas identified throughout the all samples, and most of the formulas (above 75%) were overlapped between these analyzed samples. The classification features of assigned compounds for analyzed extracts are shown in Table S2. In the assigned formulas, CHO compounds were the most abundant group, accounting for 59.2±2.2% of the total assignments, followed by CHON (35.0±2.2%). These results are consistent with previous observations of laboratory-generated biomass burning aerosol (Smith et al., 2009) and field particulate samples influenced by biomass combustion (Kourtchev et al., 2016), although the differences of biomass varieties, extracted solvent, and HRMS techniques between present and previous studies. On the other hand, CHOS and CHONS compounds contributed with less than 5% to the total assignment. A number of studies have shown the wide presence of organosulfates and nitrooxy-organosulfates in urban (Lin et al., 2012b; Wang et al., 2016), rural (Lin et al., 2012a), and forest aerosols (Kourtchev et al., 2013), and even in cloudwater (Boone et al., 2015); however, most of these compounds were not observed in our negative mass spectra. This could be accounted for by the low extent of aerosol evolution, due to the limited oxidation conditions available for the formation of

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organosulfates and nitrooxy-organosulfates in fresh smoke aerosols. For example, laboratory studies have observed the significant formation of organosulfates via photooxidation in the presence of acidic sulfate aerosol (with significant level of SO_2 concentration) (Surratt et al., 2007; Surratt et al., 2008). All detected ion species with enabled formula assignments in present samples are listed in Table S3.

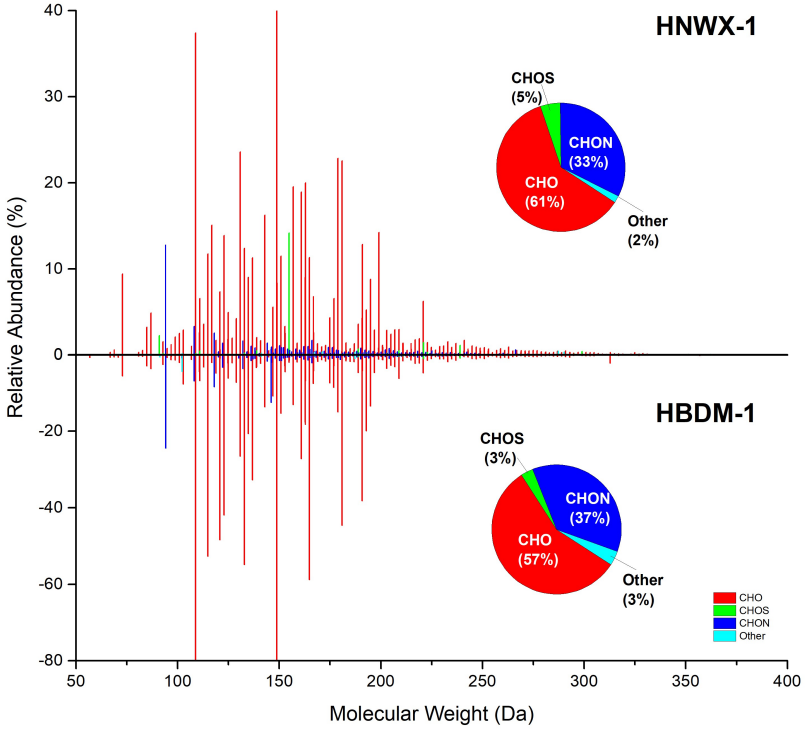

Figure 2. Reconstructed mass spectra of HNWX-1 and HBDM-1 sample. The inset pie charts show the number fraction of each class in the total assigned compounds.

The negative ion mode is prone for the detection of molecules containing polar functional groups (e.g., -OH and –COOH). It should be noted that the formula numbers detected in the HRMS potentially contain multiple structural isomers;

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255 therefore, the actual number of water-soluble organic species might be
256 underestimated. The additional LC/ESI-HRMS analysis operated in negative mode
257 confirmed a substantial number of ion masses (e.g., assigned CHO and CHON
258 compounds) containing more than one structural isomer, which could be observed at
259 different retention times (RTs) in chromatograms. Two representative groups of
260 extracted chromatograms for CHO ($[C_7H_5O_n]^-$, (n=2~4)) and CHON ($[C_7H_5O_nN]^-$,
261 (n=1~3)) compounds are shown in Figure S2 and S3, respectively, where increasing
262 the O or N atom number in a molecule might lead to more isomer peaks. However, it
263 should be noted that these LC-separated peaks might also include other unidentified
264 compounds that were outside of the elemental assignment considered in this study.
265 Additionally, low content and potential decomposition under the ionization can also
266 limit the detection of some high molecular weight species.

267 The interpretation of the complex organic mass spectra generated by high
268 resolution mass spectrometry can be simplified by plotting the hydrogen to carbon
269 ratio(H/C) against the oxygen to carbon ratio (O/C) for individual assigned atomic
270 formulas in form of the Van Krevelen (VK) diagram (e.g. Lin et al., 2012a;
271 Kourtchev et al., 2013). Figure 3a indicates a representative VK diagram of CHO
272 and CHON compounds derived from HBDM-1 sample. It can be clearly seen from
273 Figure 3a that the majority of CHO and CHON molecules are located at the region of
274 O/C$\leqslant$1.0 and H/C$\leqslant$2.0. In VK diagram, molecules with H/C$\leqslant$1.0 and O/C$\leqslant$0.5
275 are typical for aromatic species, while molecules with H/C$\geqslant$1.5 and O/C$\leqslant$0.5
276 would be associated with typical aliphatic compounds (Mazzoleni et al., 2012;

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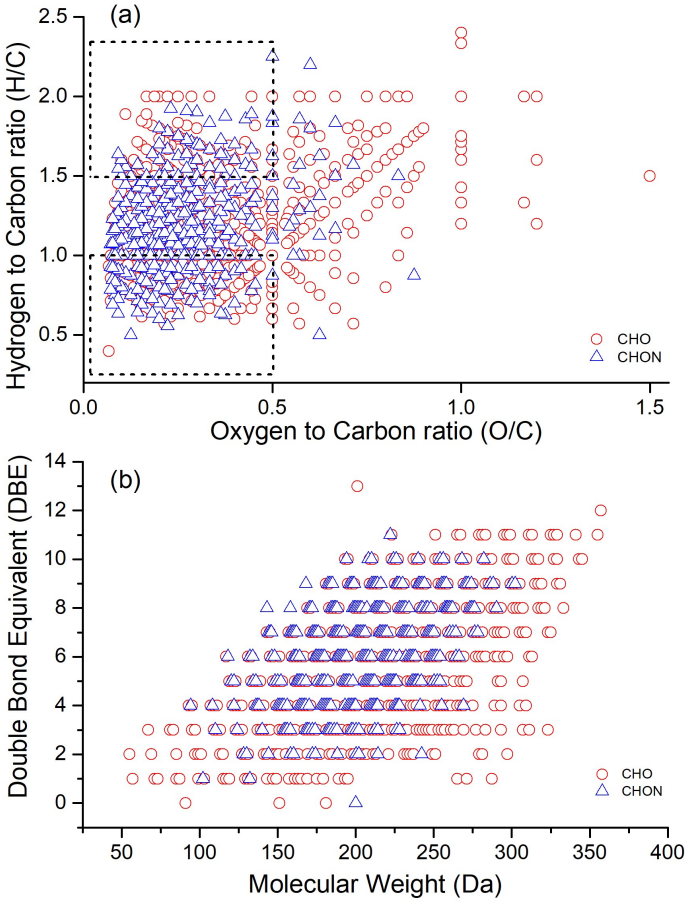
277 Kourtchev et al., 2014). The average double bond equivalent (DBE) showed relative
278 high values with 5.5 for CHO compounds and 6.1 for CHON compounds (Table S2),
279 suggesting that oxidized aromatic compounds were abundant in the present sample,
280 and their presence could partially account for the strong light-absorbing feature in
281 the near-UV region as observed in our previous study (Cai et al., 2018). Figure 3b
282 shows the distribution of molecular formulas with various DBE and indicates a large
283 number of molecular species with high unsaturation degree (DBE⩾4).



284
285 **Figure 3. VK diagram (a) and DBE vs. molecular weight (b) of CHO and CHON**
286 **compounds for one representative sample (HNDM-1).**

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The average H/C and O/C ratios throughout the all extract samples were in the ranges of 1.26-1.31 and 0.34-0.42 for CHO compounds, 1.19-1.23 and 0.28-0.29 for CHON compounds (shown in Table S2), respectively. Although the ESI analysis were performed in the negative ionization mode, the emerged O/C ratios exhibit rather low values, which fall in the range of O/C ratios typical for biomass burning organic aerosol derived from positive ionization mode (Aiken et al., 2008; Kourtchev et al., 2016). Due to fresh emission and smaller aging effect, the present O/C were obviously lower than the O/C of long-range transport biomass burning aerosols (Zhang et al., 2018).

Carbon oxidation state (OS_c) was observed to increase with oxidation for atmospheric organic aerosol and link strongly to aerosol volatility (Kroll et al., 2011). OS_c for each molecular formula can be calculated using the following equation:

$$OS_c = -\sum_i OS_i \frac{n_i}{n_c}$$

where OS_i is the oxidation state associated with element i and n_i/n_C is the molar ratio of element i to carbon within the molecule (Kroll et al., 2011; Kourtchev et al., 2013).

Figure 4 shows an overlap in OS_c plots of CHO compounds for two representative samples (HNWX-1 and HBDM-2) derived from different sampling sites. It can be seen that OS_c ranges mainly from -1.5 to +1 with an average of 0.4. Consistent with previous studies (Kroll et al., 2011; Kourtchev et al., 2016), the majority of molecules with $OS_C<0$ (low oxidized organics) and carbon atoms (n_C) lower than 20 are suggested to be associated with the primary organic aerosols emitted from biomass burning. A minor fraction of molecular formulas with $OS_C \geqslant 0$ values might be

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associated with semivolatile and low-volatility oxidized organic aerosols (Kroll et al., 2011).

A similar trend of OS_c values versus carbon number was obtained in previous studies focused on the molecular composition of organic aerosols in urban area (Wang et al., 2017) and at a road tunnel site (Tong et al., 2016), although the formulas of the specific molecular products observed from different precursors in both studies are quite different.

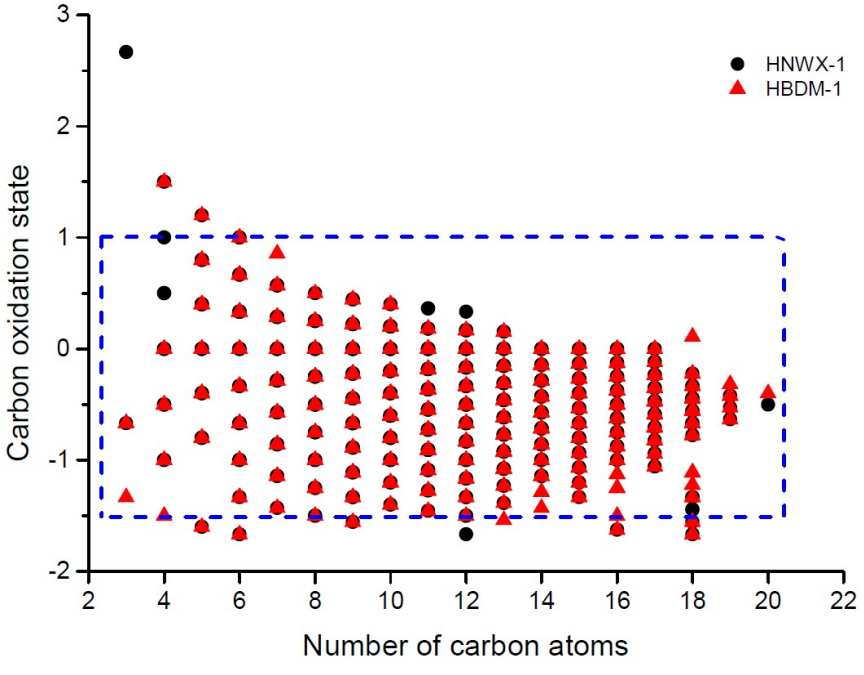

Figure 4. Carbon oxidation state (OS_C) vs. number of carbon atoms in CHO molecules.

3.2 Photochemical oxidation of phenols under laboratory conditions

Phenol and guaiacol were chosen as two representative model compounds derived from biomass combustion. Two high resolution mass spectra of aqueous phenol and

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guaiacol exposed to OH radicals for 4h, are shown in Figure S4. In Figure S4, 435 $C_xH_yO_z$ molecular formulas (m/z 90-500) were assigned for product ions of phenol (with C_3-C_{24}), whereas 624 $C_xH_yO_z$ formulas (m/z 90-600) were assigned for product ions of guaiacol (with C_3-C_{27}). The average H/C and O/C ratios were 0.79±0.28 and 0.52±0.23 for phenol, and 0.88±0.24 and 0.59±0.24 for guaiacol, respectively. Clearly, the photochemical processing induced by OH oxidation resulted in an increase in O/C of product molecules relative to their precursors (O/C=0.17 for phenol and O/C= 0.29 for guaiacol). Meanwhile, the average OS_C of products for phenol (OS_C = -0.7) and guaiacol (OS_C= -0.6) photooxidation were +0.2 and +0.3, respectively, showing an increase with oxidation. The later implies that potentially the phenols and methoxyphenols might undergo photochemical aging and thus alter the nature of primary organic aerosols (Huang et al., 2018).

The formation mechanisms of series of oxygenated products, e.g., phenolic oligomers, hydroxylated phenolic species, ring-opening and highly oxygenated compounds, are proposed in the literature (e.g. Sun et al., 2010; Chang and Thompson, 2010, Yu et al., 2014). The OH-initiated reactions would result in enhanced hydroxylation of the aromatic ring as well as to increased yields of carboxylic acids and toxic dicarbonyl compounds (Sun et al., 2010; Yu et al., 2014; Prasse et al., 2018). For example, some highly oxygenated C_2-C_5 aliphatic compounds (e.g., $C_2H_2O_4$, $C_3H_4O_4$, $C_4H_6O_4$, and $C_5H_6O_5$) corresponding to carboxylic acids (Yu et al., 2014) were clearly observed in the mass spectra of present photochemical products. The presence of these oxygenated products not only

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directly increased the degree of oxygenation in the bulk solution composition, but also contributed to the variation of solution acidity. The pH measurements indicated that the acidities ($[H^+]$) of the bulk solution increased by $(2.96\pm0.15)\times10^{-5}$ M and $(4.26\pm0.16)\times10^{-5}$ M for phenol and guaiacol, respectively.

The oligomerization induced by photochemical transformation of phenolic substances is an important formation pathway for the low-volatility, light-absorbing compounds (Smith et al., 2016). Here, phenolic dimmers (i.e., $C_{12}H_{10}O_2$ for phenol dimer and $C_{14}H_{14}O_4$ for guaiacol dimer) and higher oligomers (e.g., $C_{18}H_{14}O_3$ and $C_{24}H_{18}O_4$ for phenol trimer and tetramer, $C_{21}H_{20}O_6$ for guaiacol trimer), as well as their hydroxylated species were observed. The formation mechanism, can be ascribed to C-O or C-C coupling of phenoxy radicals that were formed via H-abstraction of the phenols or OH addition to the aromatic ring (Net et al., 2009, Sun et al, 2010). The reaction at the para position or para-para coupling was more likely to occur due to a higher probability of free electron to occur in this position (Lavi et al, 2017) or a weaker steric hindrance in the para position. The extracted LC diagrams of m/z 185.0608 and 245.0823 are shown in Figure 5a and Figure 6a, respectively, where both ions involve dimers of phenol and guaiacol with several structures, and/or other isomers. The presence of guaiacol dimer and syringol dimer was previously observed in aerosol samples largely affected by wood combustion. Based on the Aerosol Mass Spectrometer (AMS) analysis, these two dimers were suggested as markers of biomass burning aerosols (Sun et al., 2010; Yu et al., 2014). In the composition of present biomass burning aerosols, the phenolic dimers (m/z

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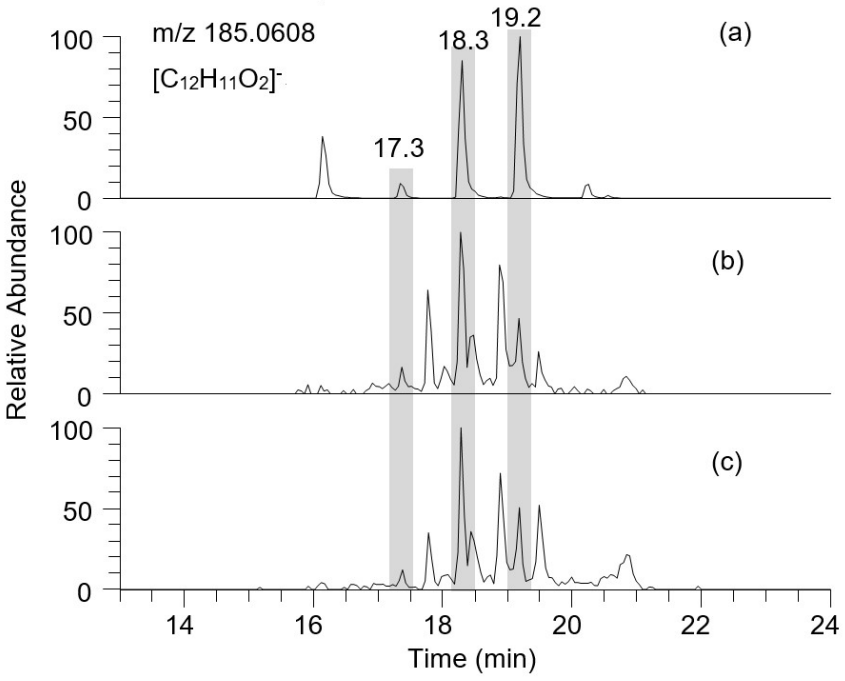
364 185.0608 and 245.0823) were also observed in present mass spectra, but the
365 extracted LC diagrams shown in Figure 5b-c and Figure 6b-c indicate that these ions
366 contain multiple RT peaks. The same peaks with RT18.3 and 19.2 min which are
367 assumed to be the phenol dimers were observed during the photochemical
368 transformation of phenol (Figure 5a) and in the straw-burning samples (Figure 5b-c).
369 Meanwhile, the present particle extracts may also involve guaiacol dimer, since its
370 m/z 245.0823 has two LC peaks emerged at RT 17.7 and 19.5 min (Figure 6b-c)
371 same as the peaks identified during the photochemical transformation of guaiacol
372 (Figure 6a).



373
374 **Figure 5. Extracted LC chromatograms of m/z 185.0608 in (a) photochemical sample of**
375 **phenol, (b) HNWX-1, and (c) HBDM-2.**
376
377 Typical hydroxylated species such as, e.g., $C_2H_2O_4$, $C_6H_6O_2$, $C_7H_6O_3$, $C_7H_8O_3$,

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were also found in the samples emerged from the photooxidation of both phenols and the straw-burning samples. The comparison of the photooxidation products stemmed from the phenols and the straw-burning samples revealed their significant difference, pointing to the importance of studying real aerosol samples against the laboratory model compounds. However, evaluating the model compounds as proxy of real aerosol samples is always helpful as a reference. To this end, it is worth noting that potentially other phenols and methoxyphenols (e.g., acetosyringone, vanillin) that dissolve into cloud, fog droplets or aerosol liquid water can be photochemically transformed and contribute to the SOA formation (Vione et al., 2019, Zhou et al., 2019).

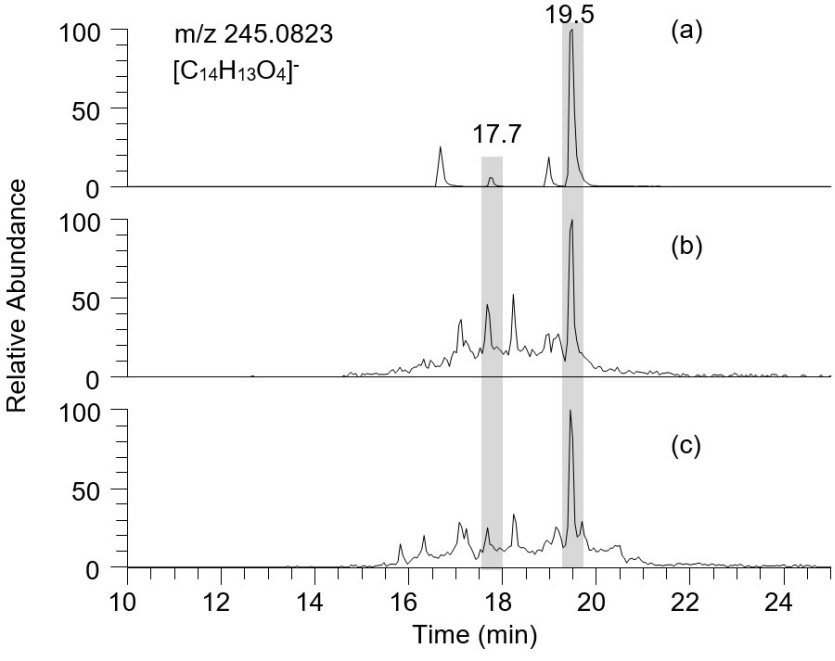

Figure 6. Extracted LC chromatograms of m/z 245.0823 in (a) photochemical sample of guaiacol, (b) HNWX-1, and (c) HBDM-2.

3.3 Photochemistry of aqueous extracts derived from straw burning aerosols

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Although the direct photolysis was performed on present straw burning samples in presence of simulated sunlight irradiation without adding any oxidants, the photooxidation process still occurred since the particle extracts were very likely to include various oxidants, e.g., singlet molecular oxygen ($^1O_2$), peroxides, hydroxyl radical (OH) or excited triplet state of organics produced under light excitation (Anastasio et al., 1997; Vione et al., 2006; Net et al., 2009; Net et al., 2010; Bateman et al., 2011; Rossignol et al., 2014; Smith et al., 2014; Gómez Alvarez et al., 2012). In particular, the excited triplet state of aromatic carbonyls (e.g., 3, 4-dimethoxybenzaldehyde) was found to be more efficient than OH radical to oxidize phenols and produce hydroxylated species (Smith et al., 2014., Yu et al., 2014). This photosensitized reaction is likely to play an important role in the WSOC evolution, due to high quantities of aromatic carbonyls present in the extracts of biomass burning aerosols.

Although no available standards were utilized for absolute quantification, the variation in peak abundance at unique retention times in the chromatogram could reflect the extent of evolution of WSOC molecules, with accurate molecular weights. The LC/ESI-HRMS monitors changes in the molecular features of a part of the WSOC, i.e., photodegradation of low oxygenated compounds and formation of high oxygenated compounds. Table 1 lists the CHO compounds for which the LC peak intensities significantly increased and decreased after the 12-hour photolysis.

3.3.1 Photodegradation of low oxygenated compounds and formation of highly oxygenated compounds

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As shown in Table 1, ion masses assigned with high unsaturated and low oxygenated species (O/C＜0.5) are prone to photodegradation, especially C_7-C_9 compounds (possible aromatic species), which intensity decreased by nearly one order of magnitude. For example, for m/z 123.0450 ($[C_7H_7O_2]^-$), as shown in Figure 7a, the peaks at RT 16.2 and 16.7 min in the LC chromatogram reduced in area by 95% after the 12-h irradiation. Using a standard it was verified that both peaks did not belong to guaiacol (peak at RT17.3 min), but they were also found within the products of guaiacol photo-oxidation, suggesting that they might be isomers of guaiacol or aromatic dihydric alcohol.

Table 1. *M/Z* with significant changes upon 12-h photolysis analyzed by LC/ESI-HRMS.

Precursor (LC peak intensity decreases by ＞50%)			Product (LC peak intensity increases by ＞50%)		
Retention time, min	Measured *m/z*	Molecular formula	Retention time, min	Measured *m/z*	Molecular formula
16.2,16.7	123.04497	$C_7H_8O_2$	1.9	59.01362	$C_2H_4O_2$
13.9,14.5	129.05555	$C_6H_{10}O_3$	1.8	72.99291	$C_2H_2O_3$
14.6	131.07121	$C_6H_{12}O_3$	2.1	73.02928	$C_3H_6O_2$
14.6	133.02934	$C_8H_6O_2$	1.8	75.00856	$C_2H_4O_3$
15.9	135.04498	$C_8H_8O_2$	2.4	85.02930	$C_4H_6O_2$
13.7	137.02426	$C_7H_6O_3$	1.9, 4.4	87.04496	$C_4H_8O_2$
17.7	137.06063	$C_8H_{10}O_2$	1.9	88.98785	$C_2H_2O_4$
15.8	147.04504	$C_9H_8O_2$	1.9	89.02427	$C_3H_6O_3$
17.2	149.06062	$C_9H_{10}O_2$	2.2	99.00857	$C_4H_4O_3$
19.0	151.07634	$C_9H_{12}O_2$	2.5	129.01917	$C_5H_6O_4$
16.8	161.06068	$C_{10}H_{10}O_2$	2.0	145.01407	$C_5H_6O_5$
16.2	165.05559	$C_9H_{10}O_3$	1.9	147.02971	$C_5H_8O_5$
14.9	167.07129	$C_9H_{12}O_3$	14.9	155.03482	$C_7H_8O_4$
15.1	181.05048	$C_9H_{10}O_4$	15.1	169.01411	$C_7H_6O_5$
17.3	191.03498	$C_{10}H_8O_4$	16.4	183.02980	$C_8H_8O_5$
16.2	195.06622	$C_{10}H_{12}O_4$			
18.6	207.06635	$C_{11}H_{12}O_4$			

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425 The phenolic dimers ($C_{12}H_{10}O_2$ and $C_{14}H_{14}O_4$) as described above also exhibited a
426 decreasing tendency with almost complete disappearance after 12h direct photolysis.
427 Other species with relatively high MW (⩾200Da) were also observed to be
428 decomposed, including m/z 251.0564 ($[C_{12}H_{11}O_6]^-$), 313.0724 ($[C_{17}H_{13}O_6]^-$), and
429 329.0674 ($[C_{17}H_{13}O_7]^-$) (Figure S5), although their initial abundance was not very
430 high.

431 On the other hand, the solution acidity ($[H^+]$) of the particle extracts increase after
432 the 12-hour photolysis, similar to the observation on the photo-oxidation of phenols
433 (section 3.2) that resulted in the formation of oxygenated species. The solution
434 acidity ($[H^+]$) normalized by WSOC concentration ($[OC_{ws}]$) was increased with a
435 variation of $\Delta[H^+]/ [OC_{ws}]=(3.8\pm0.8)\times10^{-7}$ mol mgC^{-1}, suggesting the formation of
436 new acidic substances.

437 The photochemical processing has led to an increased formation of low MW
438 compounds (e.g., C_2-C_5 species), with a relatively high O/C ratio. For example, the
439 C_2 compounds, including $[C_2H_1O_3]^-$, $[C_2H_3O_3]^-$, $[C_2H_3O_2]^-$, and $[C_2H_1O_4]^-$ (Figure
440 S6), which may correspond to glyoxylic acid, glycolic acid, acetic acid, and oxalic
441 acid, respectively, were likely to be formed via oxidation pathway of several
442 water-soluble molecules with photochemical reactivity (e.g., glyoxal (Carlton et al.,
443 2007; Lim et al., 2010), methylglyoxal (Altieri et al., 2008; Lim et al., 2010),
444 pyruvic acid (e.g. Grgic et al., 2010; Griffith et al., 2013; Reed Harris et al., 2014;
445 Rapf et al., 2017; Eugene and Guzman, 2017, Mekic et al., 2018), phenols (Sun et al.,
446 2010), etc). The presence of these highly oxygenated compounds that possibly

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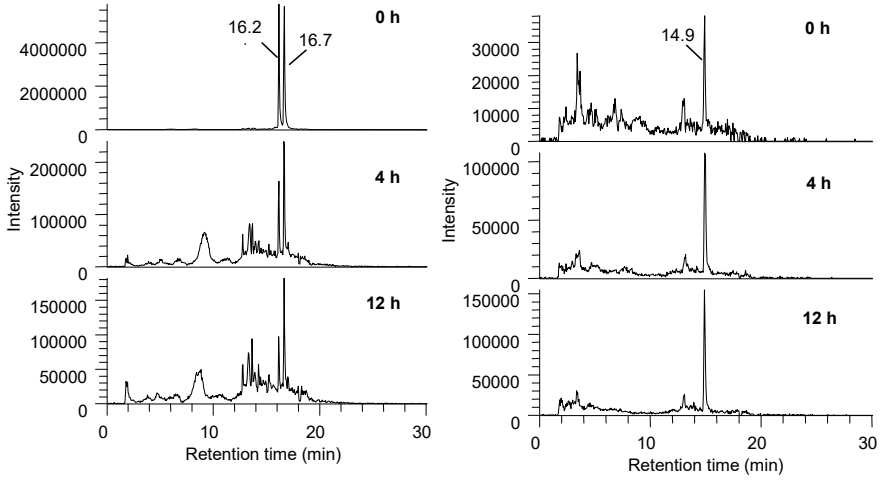
447 contain acidic groups (e.g., –COOH and –OH) undoubtedly contributed to the
448 increase of the solution acidity. Higher levels of other highly oxygenated species
449 such as $[C_3H_5O_3]^-$, $[C_4H_7O_2]^-$, $[C_5H_5O_5]^-$ and $[C_5H_7O_5]^-$ were also observed (Figure
450 S7).

451 To identify the impact of photolysis on the evolution of specific WSOC, the ions
452 of $[C_7H_7O_n]^-$ in the HBDM-1 sample with significant variation were chosen as
453 representative cases for description. The relative intensity of $[C_7H_7O_2]^-$ and
454 $[C_7H_7O_3]^-$ decreased dramatically, while the intensities of $[C_7H_7O_4]^-$, $[C_7H_7O_5]^-$ and
455 $[C_7H_7O_6]^-$ increased with photolysis (Figure 7 just shown the variation of $[C_7H_7O_2]^-$
456 and $[C_7H_7O_4]^-$). It seems reasonable that the possible hydroxylation of $[C_7H_7O_2]^-$ and
457 $[C_7H_7O_3]^-$ might contribute to the formation of $[C_7H_7O_5]^-$ and $[C_7H_7O_6]^-$. Although
458 we could not verify this hypothesis, the formed oxidized species undoubtedly have a
459 high O/C ratio which highlights the possibility of this reaction pathway.



460

461 **Figure7. Extracted LC chromatograms from HBDM-2 of (a) $[C_7H_7O_2]$ and (b) $[C_7H_7O_4]^-$ at**
462 **different photolytic stages of 0, 4, and 12 h.**

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463 **3.3.2 Effect of photolytic processing on other WSOC**

464 Some of the detected organic species exhibit a good photochemical stability, as
465 their relative intensities only slightly decreased (＜10%) after 12h light irradiation.
466 The m/z 161.0454 ($[C_6H_9O_5]^-$) presented two prominent peaks at RT1.9 and 2.4 min
467 (Figure S8). The peak at RT 2.4 min was suggested to be levoglucosan, a typical
468 tracer of biomass burning aerosols (Hu et al., 2013). Its presence in the sample was
469 further confirmed with a standard compound. The relatively good photochemical
470 stability was also observed for some C_6 homolog compounds, such as $[C_6H_7O_6]^-$,
471 $[C_6H_9O_6]^-$, and $[C_6H_{11}O_6]^-$. Some other oxygenated species, such as $[C_3H_3O_3]^-$,
472 $[C_4H_5O_4]^-$, $[C_3H_3O_4]^-$, and $[C_4H_5O_5]^-$ remained relatively stable, as well.

473 Regarding the CHON compounds, only small variation of the chromatogram
474 peaks, was observed for most of the detected species. In particular, several species
475 with low O/C decreased by less than 30%, e.g., m/z 94.0297 ($[C_5H_4ON]^-$, RT 7.1
476 min), and 120.0453 ($[C_7H_6ON]^-$, RT12.2 min). Some compounds were
477 photochemically very stable as the variation of their peak intensities was less than
478 10 % upon light irradiation of the samples, e.g., m/z 118.0297 ($[C_7H_4ON]^-$, RT16.6
479 and 17.1 min), 146.0246 ($[C_8H_4O_2N]^-$, RT14.4 min), and 190.0510 ($[C_{10}H_8O_3N]^-$,
480 RT17.8 min). However, the intensities of the ion masses with relatively higher
481 degree of oxygenation was found to increase substantially (>50%), e.g., m/z
482 162.0195 ($[C_8H_4O_3N]^-$, RT 17.2 min), 198.0408 ($[C_8H_8O_5N]^-$, RT 18.0 min), and
483 242.1763 ($[C_{13}H_{24}O_3N]^-$, RT 17.9 min).

484 Another intriguing finding was that different structural isomers with the same

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485 molecular mass might have exhibited different fates upon prolonged light irradiation
486 of the samples. For example, the intensity of the peak at m/z 165.0405 ($[C_5H_9O_6]^-$)
487 decreased when it was eluted at 4.9 min, but increased at RT 1.8 min, with the
488 irradiation time (Figure S9). A simultaneous degradation and formation among
489 isomers of some CHON ion masses upon prolonged light irradiation, was also
490 observed, as was the case for the CHO compounds. For example, the m/z 108.0453
491 assigned to $[C_6H_6ON]^-$, might include hydroxy and amino groups on the phenyl ring
492 to present three possible isomers (Figure S10). During photolytic processing, the
493 intensity of the peak at RT 3.2 min increased dramatically, while there was a clear
494 decreasing tendency of the peak intensity at RT 5.5 and 12.5 min, which was
495 suggestive of possible isomerization among these isomers. Other ion masses that
496 exhibited possible isomerization included m/z 122.0610 ($[C_7H_8ON]^-$), 132.0454
497 ($[C_8H_6ON]^-$), 134.0245 ($[C_7H_4O_2N]^-$), 136.0403 ($[C_7H_6O_2N]^-$), 138.0559
498 ($[C_7H_8O_2N]^-$), 144.0453 ($[C_9H_6ON]^-$), and 152.0352 ($[C_7H_6O_3N]^-$).

499 **3.3.3 Effect of photolytic processing on mass spectral features of WSOC**

500 Since the LC method just separated a fraction of polar compounds, we tentatively
501 utilized the change of HRMS to gain more comprehensive information about the
502 WSOC evolution. We compared the time-profile (0, 4, and 12h) mass spectra with
503 each other, based on the assumption of same interference from inorganic species, and
504 the good reproducibility and stability for orbitrap MS operated under the same
505 instrumental parameter (the RSD of TIC intensity within 5%). It is well known that
506 ESI mass spectral abundances are influenced by the solution composition,

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concentration of analytes and instrumental factors (Bateman et al., 2011); hence, it is quite challenging to directly quantify the absolute concentration levels of the complex mixtures. Despite that, the photochemical degradation of WSOC compounds and corresponding formation of organic compounds can be well described by the variation of signal intensity from mass spectrometry. The average O/C and H/C ratios for CHO compounds were from 0.38±0.02 to 0.44±0.02 and 1.24±0.03 to 1.26±0.01, respectively, as the irradiation time extended up to 12h. The comparison of these time-profile mass spectra indicates that the 12-hour photolysis resulted in a significant reduction of 28±11% in the total ion abundance (S/N). Since the photolysis induced changes in abundance for most of the CHO compounds, we also calculated the intensity (S/N)-weighted average O/C (O/C_w) and H/C (H/C_w) (Bateman et al., 2011; Romonosky et al., 2015) with values ranging from 0.45±0.03 to 0.53±0.06 and from 1.32±0.09 to 1.40±0.11, respectively. Both average O/C ratios with and without intensity-weighted showed an increased tendency that indicated an elevation in the degree of oxygenation of bulk extract composition, consistent with the LC observation, i.e. formation of highly oxygenated species and the consumption of low oxygenated compounds. This result bears similarity with previous observation using ESI mass spectrometry on characterizing photochemical transformations of d-limonene in the aqueous phase as a source of SOA (Bateman et al., 2011).

4 CONCLUSIONS

This study was focused on the effect of direct photolysis on the molecular

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529 composition of actual WSOC extracted from fresh straw-burning aerosol. The
530 photooxidation of phenols in the aqueous phase under laboratory conditions
531 indicates that the phenols in real biomass burning WSOC would likely have potential
532 to experience the similar evolution to form various oxygenated compounds under
533 relevant cloudwater condition. Because the extract composition was very complex,
534 the high-resolution mass spectrometers used in this study (ESI-HRMS and
535 LC/ESI-HRMS), although advanced still had limitations in monitoring the
536 modification of molecular composition, especially for determining the potential
537 formation of compounds present at low concentrations or compounds that were
538 poorly ionized. However, a series of polar molecules were identified that changed
539 their molecular composition via photochemical evolution. In particular, the
540 degradation of low oxygenated compounds with strong photochemical reactivity and
541 the formation of high oxygenated compounds might directly result in an increasing
542 O/C ratio in WSOC. This finding indicates that the water soluble organic fraction of
543 fresh combustion-derived aerosols have the potential to form more oxidized organic
544 matter, which might partly account for the highly oxygenated nature of atmospheric
545 organic aerosols. High MW ion masses (MW≥300Da) typical for oligomers were
546 also found in the degradation products (even some with low abundance). Some CHO
547 and CHON species exhibited no significant losses (＜10%), and displayed good
548 photochemical stability, which indicates that they may also be potential candidates of
549 tracers of biomass burning aerosols.

550 **AUTHOR CONTRIBUTION**

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Jing Cai and Zhiqiang Yu designed the experiments, and Jing Cai and Xiangying Zeng carried them out. Guorui Zhi provided the straw-burning aerosol samples, Sasho Gligorovski helped perform the analysis of light irradiation. Guoying Sheng, Xinming Wang and Ping'an Peng provided some technical consultations about organic chemistry. Jing Cai prepared the manuscript with contributions from all co-authors.

ACKNOWLEDGMENTS

This study was financially supported by the National Key Technology Research and Development Program of the Ministry of Science and Technology of China (2014BAC22B04), the National Natural Science Funds of China (41225013, 41530641, and 41373131) and the Science and Technology Project of Guangdong Province, China (2014B030301060).

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