

Molecular Characterization of Water- and Methanol-Soluble Organic Compounds Emitted from Residential Coal Combustion Using Ultrahigh-Resolution Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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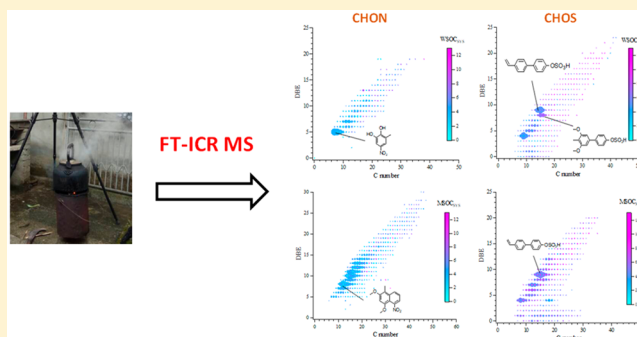
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Supporting Information

ABSTRACT: Water-soluble organic compounds (WSOC) and methanol-soluble organic compounds (MSOC) in smoke particles emitted from residential coal combustion were characterized by ultrahigh-resolution mass spectrometry. The results showed that the molecular compositions of WSOC and MSOC are different. S-containing compounds (CHOS and CHONS) are found to be the dominant components (65–87%) of the WSOC, whereas CHO and CHON compounds make a great contribution (79–96%) to the MSOC samples. It is worth noting that greater abundance of S-containing compounds was found in smoke produced from coal combustion compared to biomass burning and atmospheric samples. The molecular compositions of WSOC and MSOC also varied significantly depending on the maturity of the coal. The WSOC and MSOC derived from the combustion of low-maturity coal contained a higher proportion of oxidized functional groups but with a lower degree of aromaticity than the compounds derived from the combustion of high-maturity coal. Our findings suggest that organic molecules with a high modified aromaticity index, low O/C ratio, and low polarity showed stronger light absorption. This study also suggests that CHO and CHON compounds significantly contributed to the light absorption of WSOC and MSOC and that the contribution of CHON may be stronger.



INTRODUCTION

Brown carbon (BrC) is a type of light-absorbing organic carbon (OC) that mainly absorbs light in the low-wavelength visible and near-ultraviolet regions.^{1–6} BrC is ubiquitous in aerosols sampled from urban, rural, and marine environments,^{7–12} in smoke particles from combustion processes,^{3,13–16} and in rain, fog, and cloud water samples.^{3,17–21} BrC can not only alter the light absorption and radiative forcing of aerosols but can also influence the surface tension and formation of cloud condensation nuclei; therefore, it has a potential impact on atmospheric chemistry and climate change.^{2,4,22–25}

Numerous studies have demonstrated that atmospheric BrC can be derived from various sources, including primary emissions from biomass burning (BB),^{1,13,26–28} the combustion of fossil fuels,^{13,29,30} secondary formation via the photochemical transformation of organic compounds from BB and anthropogenic activities,^{31–34} and the oxidation of soot

particles.³⁵ In some countries, such as China, coal is still the dominant fuel for energy production. In 2015, coal consumption (4000 Tg) accounted for 68% of China's total primary energy, approximately 93 Tg of which was used as fuel for residential cooking and heating (NBSC, 2016).³⁶ Because of poor combustion conditions and a lack of emission control facilities, the use of coal for residential purposes generates huge pollutant emissions, such as OC, black carbon (BC), and polycyclic aromatic hydrocarbons.^{26,29,37–41} Recently, some relevant field and laboratory studies have been conducted to study the emission factors, abundance, and light-absorbing properties of BrC released by coal combustion.^{13,14,29} It has been found that the abundance and optical properties of BrC

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generated by coal combustion are strongly dependent on the extraction methods and the maturity of the coal. However, knowledge of the molecular properties of coal-smoke-derived BrC and the relationship to its light-absorption properties is still limited because of the highly complex composition of these substances. Therefore, further investigation is warranted.

Recently, ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has been widely used to investigate complex organic mixtures in various environments at the molecular level because of its extremely high resolution and mass accuracy.^{21,42–45} This technique allows for further exploring the molecular composition and characteristics of BrC fractions. In the present study, the extractable BrC fractions in smoke particles produced from the combustion of coal with different maturities, including water-soluble organic compounds (WSOC) and methanol-soluble organic compounds (MSOC), were characterized by FT-ICR MS coupled with negative electrospray ionization (ESI). To the best of our knowledge, this is the first detailed analysis of primary BrC fractions from residential coal combustion performed by using FT-ICR MS. The mass spectral data generated provided novel insights into the molecular nature of BrC produced by coal combustion and the influence on its light-absorbing properties.

EXPERIMENTAL SECTION

Sample Collection. In this study, four bituminous coal samples with increasing geological maturity [vitrinite reflectance (R_o), 0.55–1.3%], namely, Yulin [YL], Shuangyashan [SYS], Yongcheng-1 [YC-1], and Yongcheng-2 [YC-2] coals (Table S1), were used to produce smoke particles in a laboratory combustion and sampling system. Detailed information about these coal samples and the collection of smoke particles therefrom is presented in the Supporting Information.

Extraction of WSOC and MSOC. BrC fractions containing WSOC and MSOC were isolated from smoke particles by a solvent extraction method. Briefly, the WSOC fraction was first ultrasonically extracted with Milli-Q water from filters loaded with smoke particles and was then passed through a preconditioned Oasis HLB cartridge for desalting (Oasis HLB, Waters, Milford, USA).^{46,47} Details of the isolation method are provided in the Supporting Information and our previous paper.¹⁴ The MSOC fraction was obtained by ultrasonic extraction of filter samples with methanol (HPLC grade). The MSOC solution was filtered through a 0.22 μm poly(tetrafluoroethylene) filter and concentrated to approximately 1 mL under a gentle N_2 stream. Finally, the WSOC and MSOC extracts were stored in a refrigerator prior to analysis. Notably, the extractable WSOC and MSOC fractions accounted for 4.3–16 and 94–97% of the total carbon content in coal smoke particles, respectively, which indicated that methanol can be used to extract a much greater amount of organic compounds than water.¹⁴

UV–Vis Absorption Spectra. The UV–vis spectra for the WSOC and MSOC fractions were recorded by using a UV–vis spectrophotometer (UV-2600, Shimadzu, Japan) over the wavelength range 200–700 nm with a step size of 1 nm. Each spectrum was corrected by reference to a cuvette containing pure water or pure methanol for WSOC or MSOC, respectively. The mass absorption efficiency at 365 nm (MAE_{365}) and the absorption Ångström exponent (AAE)

were calculated (details are presented in the Supporting Information).

Ultrahigh-Resolution FT-ICR MS Analysis. The molecular characteristics of the WSOC and MSOC fractions were measured with a solariX XR FT-ICR mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 9.4 T refrigerated actively shielded superconducting magnet and a Paracell analyzer cell. The samples were ionized in the negative-ion mode using an ESI ion source, and the detection mass range was set at m/z 150–1000. The detailed analysis method is described in the Supporting Information and our previous study.⁴⁵ It is noted that the negative ESI source is more easily detecting polar compounds and that the organic molecules detected in this way form only a part of the organic compounds, which are ionized with bias in the negative ESI source.⁴⁸

RESULTS AND DISCUSSION

Mass Spectra and Molecular Formula Assignments.

Reconstructed high-resolution negative-ion ESI FT-ICR mass spectra for WSOC and MSOC in coal smoke samples are shown in Figure S1. The data obviously show that thousands of peaks are present in the spectra in the range from m/z 150 to m/z 600, and the most intense ion peaks are those in the range m/z 200–400 for WSOC and m/z 200–350 for MSOC. These ranges are similar to the ranges found for the ultrahigh-resolution mass spectra of organic compounds in smoke particles produced from the combustion of biomass materials,⁴⁵ as well as in ambient aerosols,^{42,49,50} fog water,¹⁹ rain water,⁵¹ and cloud water.¹⁷

Table S2 summarizes the number of formulae in each compound category and the average values of the molecular weight (MW), elemental ratios, double-bond equivalents (DBEs), and modified aromaticity indices (AI_{mod}) for the coal smoke-derived WSOC and MSOC. Based on the molecular formula and the abundance of each negative ion, the average molecular formulae for the WSOC and MSOC fractions from each coal variety were obtained: $\text{C}_{15}\text{H}_{17}\text{O}_{5.2}\text{N}_{0.22}\text{S}_{0.73}$, $\text{C}_{14}\text{H}_{16}\text{O}_{5.6}\text{N}_{0.26}\text{S}_{0.88}$, $\text{C}_{16}\text{H}_{17}\text{O}_{4.7}\text{N}_{0.26}\text{S}_{0.66}$, and $\text{C}_{16}\text{H}_{18}\text{O}_{4.5}\text{N}_{0.17}\text{S}_{0.66}$ for the WSOC fractions and $\text{C}_{19}\text{H}_{21}\text{O}_{3.4}\text{N}_{0.18}\text{S}_{0.23}$, $\text{C}_{20}\text{H}_{19}\text{O}_{3.9}\text{N}_{0.25}\text{S}_{0.19}$, $\text{C}_{21}\text{H}_{20}\text{O}_{2.3}\text{N}_{0.15}\text{S}_{0.05}$, and $\text{C}_{20}\text{H}_{19}\text{O}_{2.6}\text{N}_{0.20}\text{S}_{0.20}$ for the MSOC fractions derived from the combustion of YL, SYS, YC-1, and YC-2 coal samples, respectively. Notably, the average molecular formulae for the WSOC and MSOC from the same smoke sample showed some differences. The WSOC fraction had a higher relative content of O and S, whereas the MSOC fraction had a higher relative content of C and H. In addition, WSOC and MSOC derived from the combustion of low-maturity coal (YL and SYS) both had relatively high O content compared to the high-maturity coal (YC-1 and YC-2). These results suggest that the elemental composition of extractable BrC fractions was dependent on the extraction solvent and the maturity of the coal.

Based on the identified molecular formulae, four main compound groups were determined, namely, compounds containing C, H, and only O (CHO); compounds containing C, H, O, and N (CHON); compounds containing C, H, O, and S (CHOS); and compounds containing C, H, N, O, and S (CHONS). The relative abundances for the various compound groups were defined as the magnitude of each group of peaks divided by the sum of the magnitudes of all the identified peaks. As shown in Figure 1, the S-containing groups (CHOS

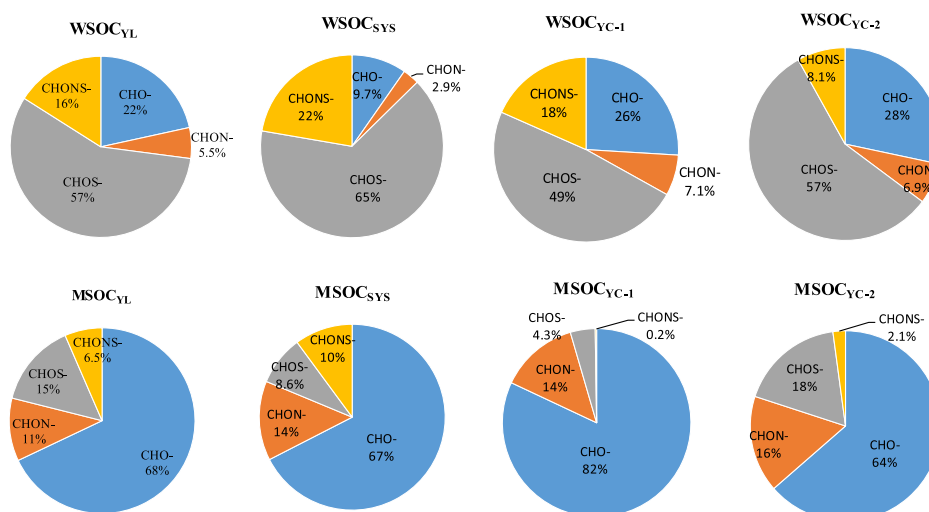


Figure 1. Comparison of the types of elemental formulae presented in the coal smoke BrC samples. The four pie charts show the percentages of different formula groups in each sample by the sum of intensity of all the identified peaks.

and CHONS) taken together constituted the major component of all the WSOC fractions, accounting for 65–87% of the overall formulae in the negative-ion mode. The CHO group was the second most abundant group (9.7–28%) and the CHON group was the least abundant group (2.9–7.1%) in the four WSOC fractions. In contrast, CHO compounds typically represented the most abundant fraction (64–82%) in the four MSOC samples. CHON, CHOS, and CHONS were present in relatively low amounts (11–16, 4.3–18, and 0.2–10%) in the total formulae of the MSOC fractions. These results clearly show that the coal smoke-derived WSOC was characterized by a high abundance of S-containing species, whereas the high abundance of CHO compounds was a distinct characteristic of coal smoke-derived MSOC. These differences may be associated with the high water solubility of S-containing compounds such as organosulfates and sulfonates.^{52,53} It was noted that the abundance of S-containing compounds in coal smoke-derived WSOC greatly exceeded that of WSOC in ambient aerosols.^{31,42} This result suggests that residential combustion of nondesulfurized coal may be an important source of water-soluble S-containing organic compounds in atmospheric samples.

As shown in Table S2, the relative-abundance-weighted MW (MW_w) values of the four compound groups in each sample were different. The CHO group had the lowest MW_w value, whereas the highest MW_w value was identified for the CHONS group, which might be due to the addition of nitrogen- and/or sulfur-containing groups to the CHO molecule or to differences in the molecular structure between CHO and CHONS. The AI_{mod} value is a measure of the C–C double-bond density and considers the contribution to π -bonds by heteroatoms, such as oxygen, sulfur, and nitrogen.⁵⁴ As shown in Table S2, the relative abundance-weighted AI_{mod} ($AI_{mod,w}$) values for the four WSOC fractions ranged between 0.32 and 0.38, which were consistently lower than the values obtained for the four MSOC fractions (0.46–0.56). This finding suggests that MSOC had higher aromaticity than WSOC, and it is consistent with observations from previous studies that most organic compounds with a high double-bond content tended to be extracted into organic solvents.^{14,55} According to previous studies, an $AI_{mod,w}$ value greater than 0.5 is a criterion for determining whether these species are

aromatic, so all the $AI_{mod,w}$ values that are lower than 0.5 may suggest that both aromatic and aliphatic species are important components for the WSOC and MSOC fractions. Furthermore, the $AI_{mod,w}$ values of each molecular group in the WSOC and MSOC fractions were also different, reflecting a similar changing trend: $AI_{mod,w}(\text{CHON}) > AI_{mod,w}(\text{CHO}) > AI_{mod,w}(\text{CHONS}) \approx AI_{mod,w}(\text{CHOS})$. This finding suggests chemical heterogeneity for the WSOC and MSOC molecules and, hence, that different compound groups may have a different influence on the chemical and optical properties of these organic materials.

Condensed aromatic hydrocarbons have been hypothesized to be derived from combustion sources and are also regarded as a marker for BC based on the elemental ratios in their molecular formulae.^{49,56} As shown in the Van Krevelen diagram (Figure S2), molecular formulae with elemental ratios typical of condensed aromatic hydrocarbons were observed in a relatively low amount for both the WSOC and MSOC fractions. A value of $AI_{mod} \geq 0.67$ has been viewed as a threshold for identifying condensed aromatic structures in molecules.⁵⁴ In this study, the percentage of condensed aromatic compounds was $15 \pm 3\%$ for the MSOC, which was considerably higher than the value of $9 \pm 3\%$ for the WSOC; this result is reasonable because condensed aromatic hydrocarbons are generally hydrophobic and, thus, make a relatively lower contribution to the highly polar WSOC. In addition, it can be noted that the relative contents of compounds with high $AI_{mod,w}$ values (≥ 0.67) in the WSOC and MSOC samples from low-maturity coal (YL and SYS) were consistently lower than those obtained from high-maturity coals, indicating that relative high contents of condensed aromatic hydrocarbons occurred in organic compounds formed from the combustion of high-maturity coal. In addition, the different compound groups contained different amounts of condensed aromatic hydrocarbons (Table S3). CHON compounds accounted for the highest proportions (20–31% of WSOC; 25–40% of MSOC) of condensed aromatic hydrocarbons, followed by CHO compounds, and the lowest content of condensed aromatic hydrocarbons was identified in the S-containing groups (CHOS and CHONS).

CHO Compounds. The CHO group is a class of compounds that probably bear carboxyl and hydroxyl functions

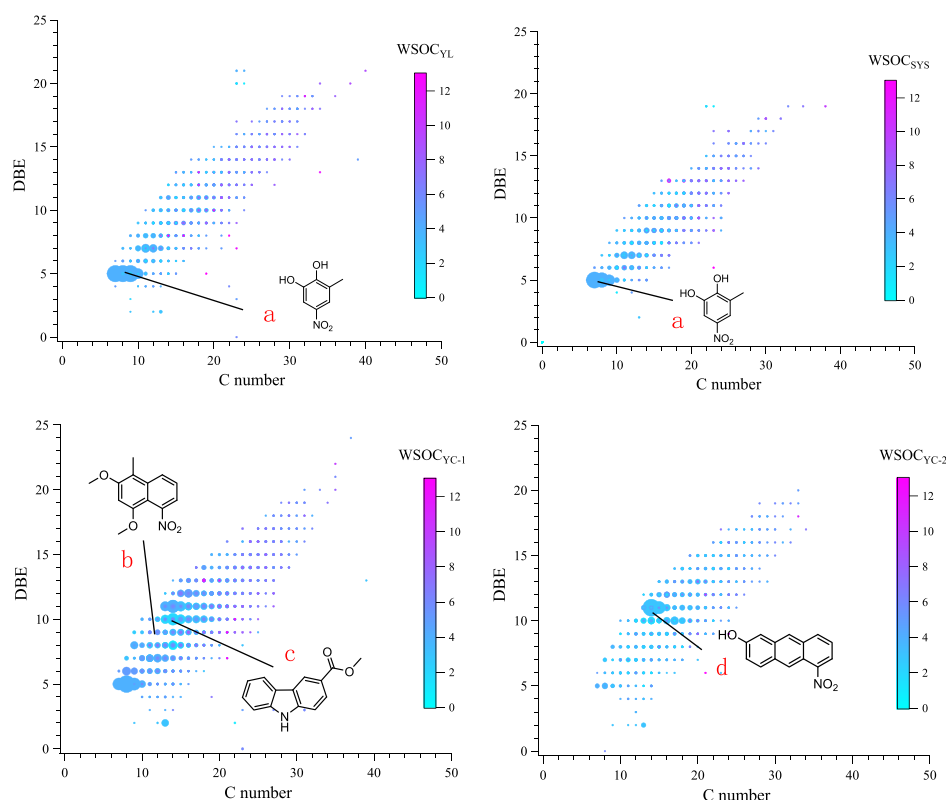


Figure 2. DBE vs C number for the CHON compounds of the coal smoke WSOC samples. The color bar and marker size denote the number of O atoms and the peak intensities of the compounds. The formulae for the compounds with high intensity (a–d) are $C_7H_7O_4N_1$, $C_{13}H_{13}O_4N_1$, $C_{14}H_{11}O_2N_1$, and $C_{14}H_9O_3N_1$, respectively. Note that the proposed structures are representative and not determined.

and is widely identified in ambient samples such as aerosols, cloud water, and rain water.^{17,31} As shown in Figures 1 and S1, CHO compounds were identified in both WSOC and MSOC, but their relative contents were very different. Approximately, 9.7–28% of the total compounds could be assigned as belonging to the CHO group from the ESI mass spectra of the WSOC fractions, which is much less than the values of 64–82% observed in the case of the MSOC fractions. As shown in Table S2, the H/C_w and O/C_w atomic ratios for CHO were 1.1–1.2 and 0.22–0.27, respectively, for the four coal smoke-derived WSOC samples. The O/C_w ratios for the coal smoke-derived WSOC samples were lower than those reported for ambient rain water (0.7 ± 0.5),⁴⁴ cloud water (0.54 ± 0.35),¹⁷ and atmospheric aerosol (0.39 – 0.54).^{17,31,42} These results indicate that the primary coal-derived WSOC samples were less oxidized than those from atmospheric samples, which may be because of further atmospheric oxidation (by $\bullet OH$, $\bullet NO_x$, O_3) of the emitted compounds in the atmosphere.^{57,58} For the smoke-derived MSOC, the H/C_w and O/C_w atomic ratios of the CHO compounds were 1.0–1.1 and 0.10–0.18, respectively. The O/C_w ratios were distinctly lower than those of the WSOC fraction from the same smoke samples, indicating that the CHO compounds in the MSOC fraction had a relatively lower content of oxidized functional groups than the WSOC fraction.

As shown in Figures S3 and S4, the DBE values for the WSOC and MSOC fractions all displayed similar changing trends with respect to the increasing C number. The DBE values and C numbers for the CHO compounds in the four WSOC fractions varied in the ranges of 0–20 and 7–32, respectively, which is lower than the ranges of 0–30 (DBE)

and 7–50 (C number) found for the MSOC fractions. These results indicate that the CHO molecules in the MSOC fraction contained many high MW compounds with a high degree of unsaturation. As shown in Figure S3, many CHO compounds in WSOC showed a C number ranging from 12 to 18, such as $C_{13}H_{18}O_4(CH_2)_{1-2}$, $C_{12}H_{10}O_2(CH_2)_{1-3}$, and $C_{13}H_{10}O_4(CH_2)_{1-3}$, which have DBE values of 5, 8, and 9, respectively. The formulae a ($C_{12}H_{16}O_4$), b ($C_{12}H_{10}O_2$), and c ($C_{14}H_{12}O_4$) appear with a high intensity and are highlighted in Figure S3, and their possible structures are also shown. These formulae probably comprise one benzene ring or a double benzene nucleus substituted with O-containing groups such as hydroxyl, methoxyl, carboxyl, and so forth. In comparison, the high intensity CHO compounds in the MSOC fraction were mainly distributed in a high C-number range (16–22) with higher DBE values (9–15). These results are consistent with the fact that high MW CHO compounds are generally characterized by relatively low polarity and poor water solubility.¹ These compounds probably comprise conjugated aromatic rings bearing polar O-containing functional groups.⁵⁷ Some possible structures for these formulae are depicted in Figure S4, including $C_{14}H_{10}O_4$ (d), $C_{18}H_{14}O_2$ (e), and $C_{20}H_{12}O_1$ (f).

CHON Compounds. CHON compounds were identified in the FT-ICR mass spectra for the WSOC fractions and accounted for 2.9–7.1% of the total number of identified formulae (Figure 1). In comparison, larger amounts (11–16%) of CHON compounds were observed in the four MSOC samples. These CHON compounds could be classified into 25 subgroups according to their N and O numbers, including O_xN_1 (O_1N_1 – $O_{13}N_1$) and O_xN_2 (O_2N_2 – $O_{13}N_2$) groups

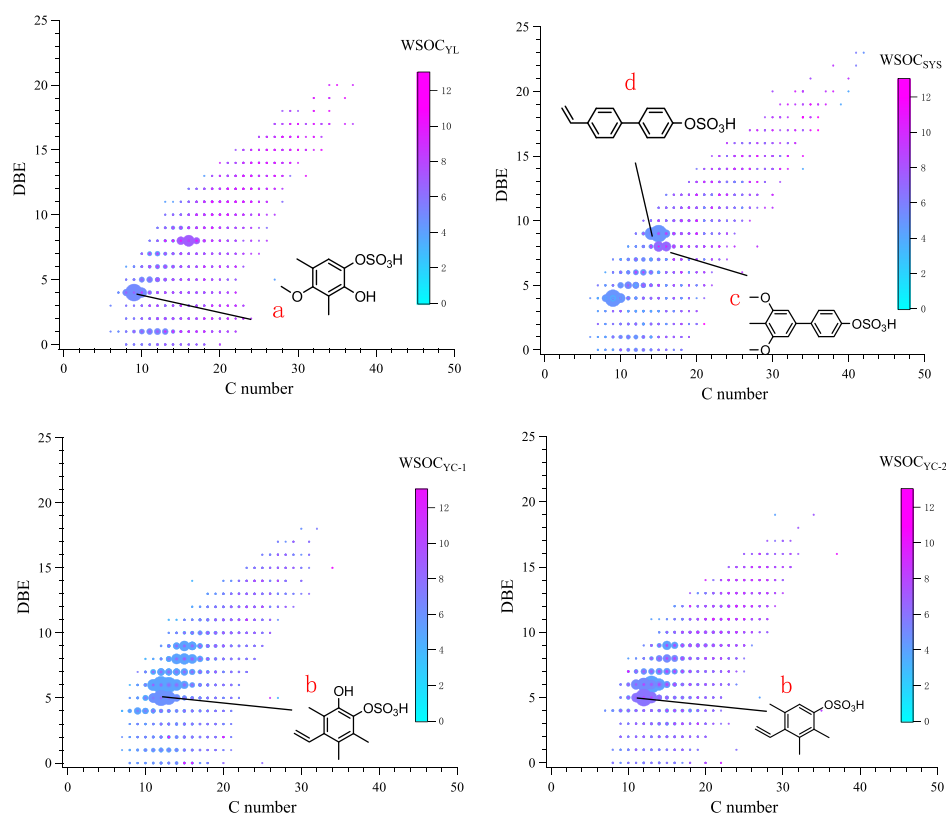


Figure 3. DBE vs C number for the CHOS compounds of the coal smoke WSOC. The color bar and marker size denote the number of O atoms and the peak intensities of the compounds. The formulae of compounds (a–d) are $C_9H_{12}O_6S_1$, $C_{11}H_{14}O_5S_1$, $C_{15}H_{16}O_6S_1$, and $C_{14}H_{12}O_4S_1$, respectively. Note that the proposed structures are representative and not determined.

(Figure S5). According to previous studies, $CHON_{O/N \geq 3}$ compounds are rich in oxygen with respect to nitrogen, which may allow for the assignment of one nitro (NO_2) or nitrooxy (ONO_2) group, resulting in nitro-substituted compounds and organonitrates candidate compounds.^{17,20,21,31,42,59} In addition, an excess of O atoms may also suggest that an amino group and other oxygenated functional groups such as hydroxyl and carboxylic functional groups are present within these compounds.³¹ In this study, the relative content of $CHON_{O/N \geq 3}$ compounds in WSOC was 66–84%, which is consistently higher than that found in MSOC (48–78%) for the same smoke sample (Table S3). These results might be due to some $CHON_{O/N \geq 3}$ compounds, such as organonitrates, having quite high polarity and water solubility.³⁴ Furthermore, the O/C_w and O/N_w ratios for the $CHON_{WSOC}$ range between 0.21–0.31 and 3.3–4.3, which are all higher than those found for $CHON_{MSOC}$ (0.11–0.21 and 2.0–3.9), and suggest that $CHON_{WSOC}$ may show a higher degree of oxidation. As shown in Table S2, the $AI_{mod,w}$ values of CHON are all higher than 0.5, and the CHON fractions in WSOC show slightly lower $AI_{mod,w}$ values compared to the MSOC fractions of the same coal smoke samples. These differences, therefore, suggest that the CHON compounds in the WSOC and MSOC fractions both comprised higher aromatic species, but a relatively higher content of aromatic compounds with a lower degree of oxidation was found in MSOC.

As shown in Table S2, CHON compounds from the low maturity YL and SYS coals showed relatively higher O/C_w and O/N_w ratios than those obtained from the high maturity coal samples. Moreover, the relative content of $CHON_{O/N \geq 3}$

compounds (with respect to the overall CHON) in the YL and SYS coal ranged between 83–84 and 73–78% for WSOC and MSOC, which is distinctly higher than that found for the high-maturity YC-1 and YC-2 coal (66–70% for WSOC and 48–56% for MSOC) (Table S3). These differences were also stressed by the distribution of highly intense CHON compounds (Figure S6). Moreover, the $AI_{w,mod}$ values for the CHON compounds increased slightly with increasing coal maturity, as indicated by Table S2. It can thus be concluded that more CHON compounds with low aromaticity and a large amount of oxidized nitrogen functional groups were formed during the combustion of low maturity coals. In contrast, the CHON compounds produced from the combustion of relatively high maturity coal were characterized by a relatively high aromaticity and a low degree of oxidation. According to previous studies, some reduced nitrogen compounds can be mainly associated with heterocyclic aromatic rings possessing a single N atom^{31,59} as well as alkyl amino and alkyl nitrile.^{59,60}

As shown in Figure 2, the CHON compounds in coal WSOC spanned a DBE range of 2–22, with the most abundant CHON species having DBE ranging between 5 and 13. In comparison, the CHON compounds in the MSOC fraction spanned a relatively wider DBE range (2–30), and the most abundant CHON species had relatively higher DBE values (7–14) (Figure S7). These results first suggest that more double bonds and/or aromatic structures occurred in the MSOC molecules. As shown in Figures 2 and S7, some high intensity formulae were detected, such as $C_7H_7O_4N_1(CH_2)_{1-3}$, $C_{10}H_9O_{3-4}N_1(CH_2)_{1-3}$, $C_{10}H_7O_{3-4}N_1(CH_2)_{1-5}$, $C_{13}H_9O_{1-3}N_1(CH_2)_{1-5}$, $C_{14}H_9O_{3-5}N_1(CH_2)_{1-4}$, $C_{16}H_{11}O_{1-2}N_1(CH_2)_{1-3}$, $C_{17}H_{11}O_{2-4}N_1(CH_2)_{1-4}$,

$C_{19}H_{13}O_{1-4}N_1(CH_2)_{1-3}$, and $C_{20}H_{13}O_{1-2}N_1(CH_2)_{1-3}$, which have DBE values of 5, 7, 8, 10, 11, 12, 13, 14, and 15, respectively. These formulae were probably mono-, di-, and polycyclic aromatic compounds bearing nitro, carboxyl, or hydroxyl substituents, or heterocyclic aromatic compounds with a single N atom, including $C_7H_7O_4N_1$ (a), $C_{13}H_{13}O_4N_1$ (b), $C_{14}H_{11}O_2N_1$ (c), $C_{14}H_9O_3N_1$ (d), $C_{18}H_{13}O_2N_1$ (e), and $C_{20}H_{13}O_2N_1$ (f). It is evident that many more high intensity CHON formulae with high DBE values occurred in the MSOC compared to the WSOC and that high-benzene ring compounds (f) were mainly identified in the MSOC samples. Again, this finding indicates higher aromaticity for the CHON compounds in the MSOC fractions.

CHOS Compounds. In this study, CHOS compounds accounted for 49–65% of the total identified compounds in coal smoke-derived WSOC, indicating that coal combustion is an important source of water-soluble OS species in an atmospheric environment. In contrast, these CHOS compounds only accounted for 4.3–18% of the total identifiable compounds in the four MSOC samples. These differences may be due to the S-containing compounds typically being polar with high water solubility, considering that many less-polar compounds cannot be extracted by pure water. As indicated in Table S2, the H/C_w and O/C_w ratios for the CHOS compounds were higher than those obtained for the CHO compounds. The majority of the CHOS compound group (yellow diamond) lies to the right of and above the CHO compounds (red triangles) on the Van Krevelen diagram (Figure S2), indicating a higher degree of oxidation. Furthermore, the average $AI_{mod,w}$ values for the CHOS compounds ranged between 0.27–0.31 for WSOC and 0.21–0.39 for MSOC (Table S2), which is significantly lower compared to the values obtained for the CHO and CHON groups in the same respective sample. The DBE values for the CHOS compounds were also lower than those obtained for the CHO and CHON compounds in each sample. Taken together, these data indicate that the CHOS compounds were characterized, by a relatively low degree of aromaticity. Moreover, the CHOS with high $AI_{mod,w}$ values ($AI_{mod,w} \geq 0.5$) amounted to 19–20% for WSOC, which is always lower than the 21–34% found for MSOC from the same coal smoke samples, suggesting that more highly aromatic CHOS compounds were contained in the MSOC fraction.

As shown in Figure S8, the identified CHOS formulae corresponded to $O_3S_1-O_{11}S_1$ and $O_4S_2-O_{14}S_2$ species, and the most abundant CHOS species identified in coal smoke samples contained 4–8 O atoms. The O-rich CHOS fraction ($O/S \geq 4$) accounts for 90–92 and 93–95% of the CHOS compounds in the WSOC and MSOC, respectively, which suggests that most of the CHOS compounds detected by negative ESI sources in our WSOC and MSOC fractions can be potentially assigned as bearing sulfate ($-OSO_3H$) or sulfonate ($-SO_3$) groups.^{31,52} These findings are similar to those found for CHOS compounds detected in ambient aerosol samples.^{31,42,52} As shown in Figures 3, S8, and S9, most of the high intensity CHOS compounds in WSOC and MSOC showed DBE values ≥ 4 , with a number of O atoms ranging between 4 and 8. These relatively high DBE values and high O/S ratios suggest that these CHOS species were likely to be aromatic compounds, specifically, benzene nuclei with sulfate attached to a side chain or to the aromatic ring. Such compounds are usually called organosulfates, some of which [25% (408) of CHOS in WSOC] have been found and identified as important

components in secondary organic aerosols in laboratory studies^{61,62} and in ambient samples (Figure S10).^{31,42,52,53} These CHOS are generally thought to be formed from the oxidation of biogenic volatile organic compounds (VOCs) (e.g., isoprene, α -pinene, limonene, and so forth.) and their oxidation products in the presence of high acidity sulfate seed aerosols.⁶¹ However, it is noted that the CHOS compounds produced from coal combustion are liable to have higher aromaticity, which is different from the results obtained by Tao et al. (2014). The latter found that the CHOS group comprised long aliphatic carbon chains and low degrees of oxidation and unsaturation in ambient air in Shanghai.⁵³

As shown in Figures 3 and S9, the high intensity formulae include $C_9H_{12}O_{4-5}S_1(CH_2)_{1-2}$, $C_{11}H_{14}O_{4-5}S_1(CH_2)_{1-3}$, $C_{11}H_{12}O_{4-6}S_1(CH_2)_{1-4}$, $C_{11}H_{10}O_{4-5}S_1(CH_2)_{1-5}$, $C_{13}H_{12}O_{4-7}S_1(CH_2)_{1-4}$, and $C_{14}H_{12}O_{4-5}S_1(CH_2)_{1-4}$, which have DBE values of 4, 5, 6, 7, 8, and 9, respectively. Among these CHOS compounds, the chemical formula $C_9H_{12}O_6S_1$ denoted (a) is consistent with an alkylbenzene ring bearing one sulfate, one methoxyl, and one hydroxyl substituent (Figure 3). The chemical formula $C_{11}H_{14}O_5S_1$ denoted (b) could correspond to an alkylbenzene ring bearing one sulfate substituent. The chemical formula $C_{12}H_{16}O_6S_1$ (e) could correspond to an alkylbenzene ring bearing one sulfate and two methoxyl substituents (Figure S9). The chemical formulae $C_{15}H_{16}O_6S_1$ (c), and $C_{14}H_{12}O_4S_1$ (d) are also highlighted in Figures 3 and S9. It is noted that some CHOS compounds in MSOC have low DBE values, and the elemental formulae for these compounds are consistent with a class of organic compounds known as linear alkylbenzene sulfonates.^{52,53}

We note that the contents of CHOS compounds with high O/S values were very similar for both WSOC and MSOC. However, some differences were observed for coal samples with different maturities. As shown in Table S2, the O/C_w and O/S_w values for CHOS in the WSOC and MSOC derived from the combustion of low maturity coal (YL and SYS) ranged between 0.34–0.42 and 5.2–5.5, which is slightly higher than the values obtained (0.28–0.36 and 4.8–5.1) from the combustion of high-maturity coal (YC-1 and YC-2). This indicates that the combustion of low maturity coal may also emit more O-rich CHOS compounds. Moreover, the $AI_{w,mod}$ and DBE_w values for the CHOS compounds in WSOC increased slightly with increasing coal maturity (Table S2). Therefore, these findings suggest that more CHOS compounds with low aromaticity and a high degree of oxidation were formed by the combustion of low-maturity coal and that the combustion of relatively high-maturity coal emitted more CHOS compounds with a relatively high aromaticity and a low degree of oxidation.

CHONS Compounds. The identified CHONS compounds accounted for 8.1–22% of the total compounds of the WSOC and for 0.24–10% of MSOC. It is noted that the relative contents of these compounds were very small in YC-1 and YC-2 MSOC (0.24–2.0%). Therefore, the CHONS compounds in these two MSOC samples were not investigated. In the other six groups of CHONS compounds, 34–60% of the formulae had enough oxygen (≥ 7 O) to account for the occurrence of both sulfate and nitrate functional groups, which may suggest the simultaneous presence of oxygenated nitrogen functional groups ($-NO_3$) and/or nitro-functionality; these CHONS compounds were probably nitrooxy-organosulfates (nitrooxy-OS).^{31,52} Some of these CHONS compounds have in fact elemental formulae consistent with nitrooxy-OS detected in

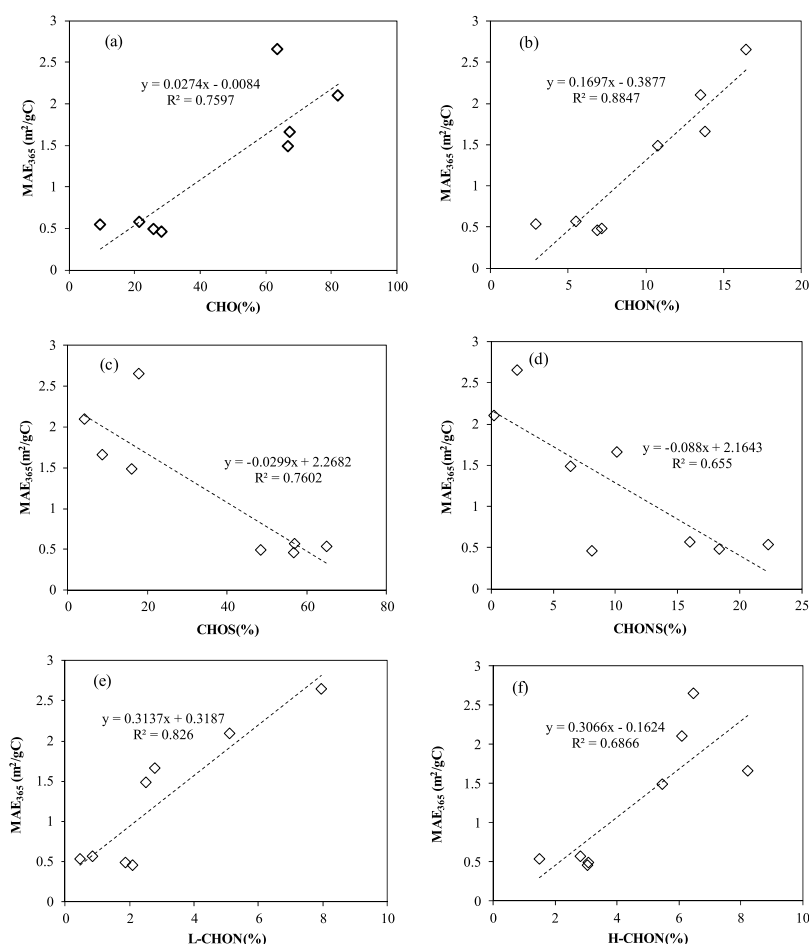


Figure 4. Correlation between the MAE_{365} values and the relative contents of CHO (a), CHON (b), CHOS (c), CHONS (d), L-CHON (e), and H-CHON (f) groups.

ambient aerosols and laboratory-based smog-chamber experiments (Figure S10).^{61,63} As reported in some studies, these nitrooxy-OS can be formed by the photochemical oxidation of VOCs in chamber experiments under high NO_x conditions.^{31,64} In a previous study, nitrooxy-OS were also identified in coal smoke-derived WSOC, but these results are based on only one type of lignite coal.⁴⁵ The data in this study suggest that the combustion of coal of any maturity may be an important source for this class of compounds. Although nitrooxy-OS could possibly occur in these samples, 40–66% of the CHONS compounds had fewer O atoms (<7) in both WSOC and MSOC. Therefore, these S-containing compounds may contain reduced S (e.g., aromatic S) or reduced N functional groups (e.g., amide, nitrile, or heterocyclic aromatics) because of insufficient oxygen content in the molecular formulae.

As shown in Table S2, the average $AI_{mod,w}$ values were 0.28–0.40 for the WSOC and 0.22–0.29 for the MSOC; these values were all less than 0.5, which is a criterion for determining whether or not they are aromatic. These results may indicate that both aromatic and aliphatic structures are important components of CHONS in coal smoke-derived WSOC and MSOC, with a prevalence of aliphatic species. As shown in Figure S11, the observed CHONS compounds were $O_4N_1S_1$ – $O_{12}N_1S_1$ and $O_6N_2S_1$ – $O_{12}N_2S_1$ species, with $O_6N_1S_1$ and $O_7N_1S_1$ being the most abundant formulae. The high intensity formulae included $C_{13}H_{25}O_6N_1S_1(CH_2)_{1-10}$,

$C_{10}H_{17}O_6N_1S_1(CH_2)_{1-13}$, $C_{10}H_{15}O_6N_1S_1(CH_2)_{1-11}$, $C_{10}H_{11}O_6N_1S_1(CH_2)_{1-6}$, $C_{12}H_{13}O_6N_1S_1(CH_2)_{1-4}$, $C_{13}H_{13}O_5N_1S_1(CH_2)_{1-4}$, $C_{14}H_{13}O_4N_1S_1(CH_2)_{1-5}$, $C_{15}H_{13}O_6N_1S_1(CH_2)_{1-5}$, $C_{18}H_{17}O_5N_1S_1(CH_2)_{1-3}$, and $C_{20}H_{19}O_5N_1S_1(CH_2)_{1-3}$, which have DBE values of 2, 3, 4, 6, 7, 8, 9, 10, 11, and 12, respectively (Figure S12). The most abundant formulae for the $O_6N_1S_1$ species were $C_{13}H_{15}O_5N_1S_1$ (a), with DBE = 7, and its isomer, $C_{13}H_{15}O_7N_1S_1$. The most likely structure was that of a quinoline ring bearing one sulfate substituent. In addition, a high abundance of the chemical formula $C_{16}H_{19}O_7N_1S_1$ (b) with DBE = 9, and isomers thereof, was also observed, which could correspond to a double benzene ring bearing one sulfate and one nitrate group.

As shown in Figure S12, some high intensity CHONS species with lower DBE values (2–3) were observed in YL and SYS MSOC, which were weaker in the WSOC isolated from the same smoke sample, possibly indicating more aliphatic species in the former. As shown in Table S2, the CHONS species in the WSOC derived from the combustion of low maturity coals had relatively low DBE_w and $AI_{mod,w}$ values and relatively high O/C_w and O/S_w values, compared with the CHONS species in the WSOC derived from the combustion of high-maturity coals. Moreover, a high content of an O-rich CHONS fraction ($O/S \geq 7$) was also observed by the combustion of low-maturity coals. These differences suggested that the CHONS species derived from the combustion of low-

maturity coal had a higher degree of oxidation, but a lower degree of unsaturation and/or aromaticity.

Correlation between Light Absorption and the Molecular Properties of Extracted Organic Compounds.

The mass absorption efficiency at a wavelength of 365 nm (MAE_{365}) is a key parameter that can be used to describe the light-absorbing ability of the different chromophores in BrC samples; here, this value was found to range between 0.54 and 0.68 m²/g C for WSOC dissolved in water, and 0.46–0.57 m²/g C for WSOC and 1.5–2.7 m²/g C for MSOC when they dissolved in methanol, as presented in Table S4. It is noted that the MAE_{365} values of MSOC were always higher regardless of the solvent. In general, the light absorption property of BrC is strongly correlated with its molecular characteristics. In the present study, the correlation between the molecular composition and light absorption of BrC in methanol was investigated, which has importance for assessing the chemical structures responsible for light absorption.

As shown in Table S5, the MAE_{365} values showed strong positive correlations with the parameters $AI_{mod,w}$ ($r = 0.926$, $p < 0.01$), DBE ($r = 0.942$, $p < 0.01$), and DBE/C ($r = 0.882$, $p < 0.01$), confirming that the light absorption of the BrC fractions is mainly affected by unsaturation and aromaticity. Moreover, negative correlations between the MAE_{365} values and the elemental atomic ratios H/C, O/C, and S/C were observed, suggesting that organic compounds with relatively low polarity show higher light absorption.^{1,6,34}

Moreover, significant positive correlations were observed between the MAE_{365} values obtained for BrC and the relative content of CHO ($r = 0.872$, $p < 0.01$) and CHON ($r = 0.940$, $p < 0.01$), indicating that both CHO and CHON groups make significant contributions to the light absorption of BrC. The MAE_{365} values also showed positive correlations with the $AI_{mod,w}$ values obtained for CHO and CHON (Table S5), further supporting this conclusion. Furthermore, the relationship with the MAE_{365} values differed somewhat between CHO and CHON. As shown in Figure 4, the plot of the MAE_{365} values versus the content of CHON had higher slope compared to the case of CHO, suggesting that the CHON species may have higher absorption coefficients than the CHO species. These data are consistent with the conclusion that N-containing compounds such as nitrophenols are important light-absorbing compounds in BrC samples.^{6,23,65–67} In contrast, the MAE_{365} values showed negative correlations with the relative content of CHOS ($r = -0.872$, $p < 0.01$) and CHONS ($r = -0.809$, $p < 0.01$). These results suggest that the CHOS and CHONS compounds have a relatively weak light-absorption capability in total organic molecules.

CHON species can be divided into aromatic N compounds ($AI \geq 0.5$) and aliphatic N compounds ($AI < 0.5$). The aromatic N compounds can be further divided into L-CHON with $O/N < 3$ and H-CHON with $O/N \geq 3$, that is, reduced N compounds (e.g., heterocyclic aromatic compounds) and oxidized N compounds (e.g., nitro-aromatics). As shown in Table S6, the MAE_{365} values exhibited a positive correlation with total aromatic CHON ($r = 0.957$, $p < 0.01$), but no correlation was observed between the MAE_{365} values and the content of aliphatic CHON. This finding suggests that aromatic CHON predominantly contributes to BrC light absorption.^{6,23} Moreover, the MAE_{365} values showed a significant positive correlation with the L-CHON content as well and a positive correlation with the H-CHON content; the slopes of these relationships are similar (Figure 4), thus

implying that both L-CHON and H-CHON make important contributions to BrC light absorption.

The absorption AAE is indicative of the wavelength dependence of BrC light absorption and is also an important parameter in climate models. As shown in Table S5, no significant correlations were observed between the AAE values for BrC and the molecular composition and characteristics of the WSOC and MSOC, implying that AAE could be influenced by many factors.

Environmental Significance. It is well known that coals used for residential combustion are generally nondesulfurised; therefore, an amount of sulfate is emitted into the atmosphere by the combustion of residential coal,^{68,69} which imposes a cooling effect on Earth's climate. This study analyzed the molecular composition of extractable organic compounds in coal smoke samples. It revealed that WSOC and MSOC both comprised CHO, CHON, CHOS, and CHONS compounds, many of which are light-absorbing organic compounds (i.e., BrC). The BrC could counteract the cooling effect of sulfate aerosols. In addition, many aging reactions, such as photochemical degradation and formation, can occur when fresh burning-derived organic compounds are emitted into the atmosphere.^{70–72} These aging processes can lead to significant changes in the light absorptivity and chemical properties of BrC materials. Thus, the optical properties and lifetimes of organic compounds emitted from coal combustion should be considered in climate models.

Organosulfates have been observed as substantial constituents in secondary organic aerosols in laboratory studies^{61,73} and in ambient organic aerosols.^{31,42,52,53,74} These compounds are suggested to be formed from atmospheric reactions of VOCs, such as isoprene, monoterpenes, and sesquiterpenes, in the presence of high acidity sulfate seed aerosols.^{61,63} However, this study shows that S-containing compounds form the major component of the WSOC fractions in coal smoke samples. Therefore, coal combustion could be an important source of atmospheric organosulfates in certain areas such as northern China, where coal is still widely used in the residential and industrial sectors and should not be neglected in future studies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b04331.

Information for the collection of smoke particles from coal combustion, extraction of water- and MSOC, total organic carbon analysis, FT-ICR MS, and light properties (PDF)

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Notes

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