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Comparison of water-soluble and insoluble organic compositions attributing to different light absorption efficiency between residential coal and biomass burning emissions

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Abstract

There are growing concerns about the climate impacts of absorbing organic carbon (also known as Brown Carbon, BrC) in the environment, however, the chemical composition and association with the light absorption ability of BrC remain poorly understood. In this study, focusing on one major source of BrC, water-soluble and water-insoluble organic carbon (WSOC; WISOC) from residential solid fuel combustions were characterized at the molecular level, and evaluated for their quantitative relationship with mass absorption efficiency (MAE). The MAE values at λ=365 nm from biomass burning were significantly higher than the coal combustion smokes. Thousands of peaks were identified in the m/z range of 150-800, with the most intense ion peaks of 200-500 m/z for WSOC and 600-800 m/z for WISOC, respectively. CHO group was the most abundant component in the WSOC extracts from biomass burning emissions compared to coals; while sulfur-containing compounds (CHOS+CHONS, SOCs) were more intense in the WISOC extracts, especially in coal emissions. Emissions of the CHON group were positively correlated with the fuel N content (r=0.936, p<0.05), which explained higher CHON emissions in coal emissions compared to biomass burning emissions. The SOCs emissions were more predominant in flaming phases, as seen from a positive correlation between SOCs and modified combustion efficiency (MCE) (r=0.750, p<0.05). The unique formulas of coal combustion aerosols were in the lower H/C and O/C regions with higher unsaturated compounds in the van Krevelen (VK) diagram. In WISOC extracts, coal combustion emissions had significantly high fractions of condensed aromatics (32-59%) which was only 4.3-9.7% in biomass burning emissions. The CHOS group in biomass burning emissions was characterized by larger condensed aromatic compound fractions compared to coal combustion. The CHOS aromatic compounds fractions were positively correlated with MAE values, in both WSOC (r=0.714, p<0.05) and WISOC extracts (r=0.929, p<0.001), suggesting the abundance of CHOS

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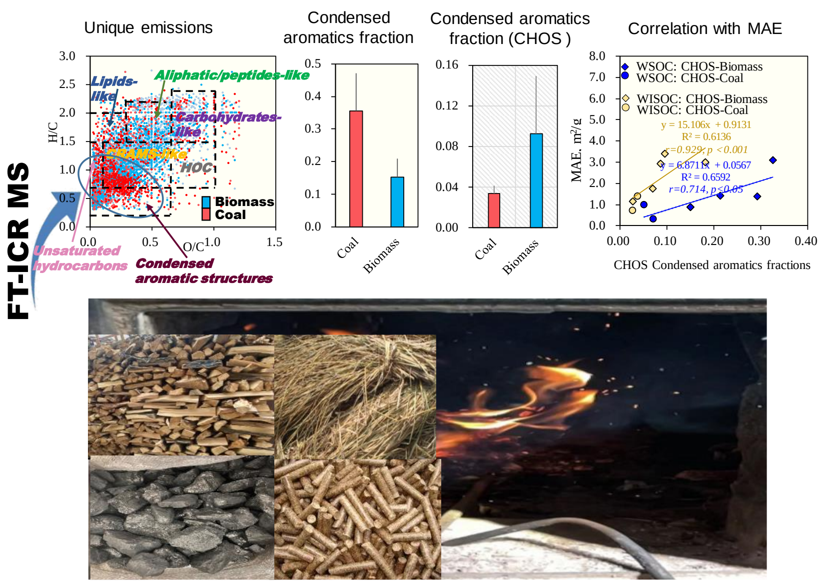
aromatic compounds explained MAE variabilities across the different fuels.

Keywords: light absorption properties, atmospheric aerosols, N-containing compounds, S-containing compounds, water-soluble compounds, water-insoluble compounds.

TOC



1. Introduction

Light-absorbing organic carbon (OC), known as Brown Carbon (BrC), attracts growing concerns due to its direct radiative impact on climate change (Laskin et al., 2015; Wang et al., 2022). The global simulations suggested that BrC may contribute nearly 20% of the surface organic aerosol (OA) burden (Jo et al., 2016), and accounted for 19% of the light absorption by anthropogenic aerosols (Feng et al., 2013). BrC can be from various sources, including primary emission sources such as coal combustion, biomass burning, and vehicular emissions (Du et al., 2014; Olson et al., 2015; Bond, 2001; Sun et al., 2017; Chen and Bond, 2010). Secondary processes such as the oxidation of volatile organic compounds would also generate considerable BrC (Guan et al., 2020; Laskin et al., 2015). Among these sources, residential solid fuel burning produce large amounts of

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BrC, accounting for 74% of the total anthropogenic primary emissions (Xiong et al., 2022).

Some efforts have been made to explore the BrC physiochemical properties in residential emissions. For example, water-soluble organic carbon (WSOC) and methanol-soluble organic carbon (MSOC) were analyzed in primary emissions from combustions of crop straw, wood fuel, and some coals (Park and Yu, 2016). Available studies suggested that the optical properties of primary BrC varied largely, being influenced by many factors, such as inherent fuel properties and combustion conditions. Mass absorption efficiency (MAE) is a key parameter in assessing direct radiative forcing of the light-absorbing carbonaceous aerosols (Huo et al., 2018). The water-soluble BrC from bituminous coals were found to have higher MAE values than anthracites (Tang et al., 2020); however, less well understood are the chemical components, at the molecular level, responsible for light absorption differences among different fuels. It was also reported that the mass absorption of water-insoluble organic carbon (WISOC) could be even greater than that of the water-soluble ones (Chen and Bond, 2010; Huang et al., 2018), but little information is available on chemical components of them. Considering that BrC light absorption varied dramatically among the different fractions and different fuels (Xie et al., 2017), detailed information of a comprehensive characterization, including the chemical and optical characteristics of the BrC fractions (including both water-soluble and water-insoluble ones) from the combustion source, is needed.

In this study, WSOC and WISOC in smoke particles produced from the burning of coals with different maturity, raw biomass fuels and biomass pellets in traditional and improved stoves were investigated for their chemical compositions and light absorption abilities. The use of biomass pellet has been heavily promoted over the last several years to mitigate air pollutant emissions from traditional solid fuels, and emission characteristics from improved stoves could be different from traditional ones. Optical property variations were quantitatively assessed and analyzed for their

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association with chemical components. Unique molecules and fingerprints for coal and biomass sources were discussed that is critical in pollution source appointment.

2. Materials and methods

2.1 Laboratory Combustion Emission Experiment

In this study, fourteen coals with different maturity, five biomass pellet, and twelve raw biomass were tested in two stoves (one traditional stove (TS) and an improve stove (IS)) in the laboratory combustion system. The thirty-four fuel-stove combinations are listed in the Table S1. The combustion tests were conducted in a designed system equipped with real-time gaseous pollutants including CO, CO_2, hydrocarbons (HC), and nitrogen oxide (NO_X including NO and NO_2) online monitor (Thermo Scientific Inc., Bremen, Germany). $PM_{2.5}$ (particles with aerodynamic diameters ≤2.5 μm) was collected at a flow rate of 16.7 L/min with the quartz filters. Fuel properties including moisture, volatile matter content (V_{daf}), ash content, lower heating value (LHV), and contents of C, H, N, and S are tested and listed in Table S1. Details of stove construction and combustion processes were available in Zhang et al., (2022). Modified combustion efficiency (MCE) was calculated by integrating the incremental concentrations of CO_2 and CO as:

$$MCE = \frac{CO_2}{CO_2 + CO}$$

where CO_2 and CO are the excess molar mixing ratios of CO_2 and CO, respectively (Pokhrel et al., 2016). The MCE values indicate different combustion phases: approximately 1 during flaming, and 0.7-0.9 during smoldering (Yokelson et al., 1997)

2.2 Bulk carbon and UV-vis Absorption Spectra

For each sample, a 4.9 cm^2 was extracted ultrasonically with 10 mL Milli-Q water (18.2 MΩ) for 30 min, and then the supernatant was separated. The extraction process was repeated twice, and

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the extracts were combined to obtain WSOC. The water extract was then filtered via 0.22 μm polytetrafluoroethylene (PTFE) filter. The insoluble PM components that remained on the sample filter were further freeze-dried and extracted with methanol via sonication and then filtered via a PTFE filter to obtain water insoluble fraction. The carbon content of WSOC was analyzed with a total organic carbon (TOC) analyzer (TOC-Lcph/cpn, SHIMADZU, Japan), and the WISOC were calculated as OC subtracting WSOC given that the methanol extraction efficiency for all combustion samples were up to 90% as proved previously (Zhang et al., 2022). The OC was measured using a thermal-optical analyzer (Sunset OC/EC analyzer) with an interagency monitoring of protected visual environments (IMPROVE) program.

The light absorption spectra of the water and methanol extracts were measured between 200 nm and 600 nm by UV–vis spectrophotometer (UV-2600, Shimadzu, Japan) at a step size of 1 nm. MAE values of WSOC and WISOC at the wavelength of λ ($MAE_{\lambda,\ WSOC}$; $MAE_{\lambda,\ WISOC}$) were calculated as following equation (Li et al., 2019):

$$MAE_{\lambda,\ WSOC}=A_{\lambda,\ WSOC}\times \ln(10)/(C_{WSOC}\times L);\ MAE_{\lambda,\ WISOC}=A_{\lambda,\ WISOC}\times \ln(10)/(C_{WISOC}\times L)$$

where $A_{\lambda,\ WSOC}$ and $A_{\lambda,\ WISOC}$ is the light absorption value of WSOC extract and WISOC extract at a wavelength of λ, respectively; C is the concentration of WSOC (or WISOC), and L is the optical path length which is 0.01 m in this study.It is important to note that the reported light absorption of WISOC in this study were underestimated, while such underestimation is insignificant due to the high extraction efficiency. In this study, the MAE values of extractable OC at λ of 365 nm ($MAE_{365,\ WSOC}$ & $MAE_{365,\ WISOC}$) were discussed.

Absorption Ångström exponent (AAE) values were determined based on the following equation (Li et al., 2019; Li et al., 2020):

$$A_{\lambda}=K_{\lambda}^{-AAE}$$

where K is a constant and AAE is obtained through the linear regression of lg (A_{λ}) against lg λ

(Fig S1). Wavelength of 300-400 nm is chosen according to the published literature (Yue et al., 2022), and the goodness of fit for all the samples in this study is greater than an r^2 of 0.99.

2.3 FT-ICR MS Analysis

The WSOC and WISOC extract from seven selected source samples were selected for further FT-ICR MS analysis. These samples included two coals (high volatile bituminous coal, HVB; medium volatile bituminous coal, MVB) combusted in TS, two raw biomass (rice straw and pine wood) combusted in TS, pine wood combusted in IS, and two biomass pellet (crop straw pellet and pine wood pellet) combusted in IS as noted in SI. Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has been successfully applied for molecular-level characterization of compounds (Bianco et al., 2018) due to its ultrahigh resolution and mass accuracy. ESI is well-adopted to characterize soluble aerosols, especially for the detection of polar, hydrophilic molecules like humic-like substances (HULIS)-type compounds (Wozniak et al., 2008), because it is a “soft” ionization technique generating minimal analyte fragments, and thus can detect intact molecules of compounds. Therefore, the negative ESI-FT-ICR was applied here to determine the molecular compositions of WSOC and WISOC from combustion samples from different solid fuels. The methanol extracts were evaporated to dryness under a gentle stream of nitrogen, and then dissolved with Milli-Q water. The WSOC and water-reconstituted WISOC were submitted to solid-phase extraction (SPE) using Bond Elut PPL (500 mg, 6 mL, Agilent, U.S.A.). Prior to the extraction, the PPL cartridges were sequentially conditioned with 12 mL methanol and 12 mL Milli-Q water containing 0.05% hydrochloric acid (HCl). The extract was adjusted to Ph=2 using HCl to remove inorganic ions and was then loaded onto the PPL cartridges at a rate of 5 mL/min. Cartridges were washed with 18 mL Milli-Q water containing 0.05% HCL to remove salt, and then dried under pure nitrogen. Analytes were eluted with 12 mL methanol, and the combined eluates were concentrated

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to 1mL. Then the molecular characterization was conducted using a 15T SolariX XR FT-ICR MS (Bruker Daltonik GmbH, Bremen, Germany) in the negative ESI mode (ESI−). The capillary inlet voltage was set at -4.0 kV and ion accumulation time was set to 0.06 S. There were 300 continuous 4 M data FT-ICR transients added to improve the signal to noise ratio. The FT-ICR MS was calibrated with 10 mmol/L sodium formate in advance, and internal standard calibration with soluble organic matter (known molecular formula) was performed after the test. Finally, <1 ppm absolute mass error was achieved. Data processing details are described in the Supporting Information (SI).

3. Result and discussion

3.1 Optical characteristics of WSOC and WISOC

MAE is an important parameter reflecting the light absorption capability of the carbonaceous aerosols. The $MAE_{365, WSOC}$ of aerosols from residential source in this study ranged from 0.21 to 3.1 m^2/g with an average of 1.3±0.7 m^2/g. MAE values of extractable OC in this study was lower than that of 11.3 m^2/g for pure BC aerosols (Bond and Bergstrom, 2006) and also lower than that from the filter-based MAE values of OC of 0.16-13 m^2/g from residential sources (Zhang et al., 2021b). A significant difference (p<0.05) of $MAE_{365, WSOC}$ was observed among the different fuels (Fig.1). The $MAE_{365, WSOC}$ of raw biomass combustion derived aerosols averaged at 1.7±0.8 m^2/g, which was significantly higher (p<0.05) than those from coal smoke (0.93±0.44 m^2/g) and biomass pellet smoke (1.2±0.6 m^2/g). The $MAE_{365, WISOC}$ was in the range of 6.6±0.5 m^2/g and at the average of 2.0±1.3 m^2/g. Obviously, the absorption capability was higher for the WISOC extract than the WSOC extract. This is thought to be associated with distinct chemical compositions of light-absorbing organics. It was noted that the WISOC had higher MAE values compared to the WSOC, which may be explained by the more hydrophobic PAHs and quinones (Chen and Bond, 2010). The difference of $MAE_{365,\ WISOC}$ among the different fuels was also statistically significant (p<0.05), as the value obtained from raw biomass burning (2.8±1.4 m^2/g) was significantly higher than that from coal combustion (1.2±0.6 m^2/g). The MAE values of soluble OC were dependent on the chemical composition of OC, that is, the chemical structure of the light absorbing chromophores and the ratio of non-light-absorbing organics to the chromophore components. The higher MAE values of raw biomass combustion derived aerosols might be caused by stronger light absorption capability of chromophores or higher ratio of chromophores. Our result was comparable to the published data, for example, the $MAE_{365,\ WSOC}$ was reported to average at 1.37±0.23 m^2/g for biomass burning emissions (Park and Yu, 2016). The correlation of MAE with the MCE was investigated. The variability in MAE values, for both WSOC and WISOC, was observed to be negatively correlated with the MCE (or temperature as MCE was found to be positively correlated with the measured temperature in emission exhausts), when pooling all data together as seen in Fig. 1C and 1D. However, within each fuel group, there was no statistically significant correlation between the MAE and MCE values (Fig. S2). Some previous studies found that OC from wood pyrolysis under higher temperature conditions had stronger absorption capability (Chen and Bond, 2010; Saleh et al., 2014), but relatively higher mass absorption coefficient (MAC) values were also reported for the organic aerosol from wood combustion under the 150°C < T < 250°C compared to emissions at a lower (T < 150°C) or higher (250°C < T < 380°C) temperature condition (Rathod et al., 2017). Chen et al., (2010) reported that that absorption per mass (α/ρ) of methanol extracts increased with increased wood pyrolysis temperature, but such increase was nonlinear and varied in burning emissions of different fuel types or wood with different sizes. Therefore, the apparently negative correlations between MAE and MCE values when pooling all data together in Fig. 1 were from distinct absorption properties of emissions from different fuel types, rather than the conditions like combustion temperature.

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The AAE which indicates the wavelength dependence of light absorption is also an important parameter in climate models. The calculated AAE in the WSOC extract (AAE_{WSOC}) ranged from 3.8 to 11 with an average of 6.9±1.5, and the difference of AAE_{WSOC} values among the different fuels was statistically significant ($p < 0.05$) (Fig.1). The highest values were observed for the aerosols from raw biomass combustion of 7.5±1.4, followed by coal smoke of 6.7±1.5 and biomass pellet smoke of 5.6±1.2. The AAE values in the WISOC extract (AAE_{WISOC}) were slightly lower than AAE_{WSOC}, which ranged from 4.2 to 6.5 with an average of 5.5±0.5. The aerosols from biomass burning impact area was also reported to have higher AAE_{WSOC} of 6.8 ± 0.98 than AAE_{WISOC} of 5.8 ± 1.0. The differences of AAE_{WISOC} values among the different fuels were statistically insignificant ($p > 0.05$), with averaged values of 5.8±0.3 for coal smoke, 5.1±0.9 for biomass pellet smoke, and 5.2±0.4 for raw biomass smoke. There was a weak positive correlation of AAE_{WISOC} between the MCE values ($p<0.05$). The filter-based analysis also showed that AAE values were positively correlated with MCE values, indicating that more BrC were produced under smoldering phase compared with BC (Zhang et al., 2020). This study suggested that soluble BrC was apt to be generated during the smoldering phase in comparison with the non-light-absorbing OC. The AAE values in soluble OC in this study were higher than 4 for all samples, confirming the contribution of BrC to aerosol absorptivity from source emission. The result of this study was comparable to the published literature. For example, it was reported that the AAE_{WSOC} was in the range of 8.6-15 from coal combustion derived aerosols (Song et al., 2019), and 6.2-9.3 from biomass smoke (Park and Yu, 2016). The AAE_{WISOC} from wintertime urban aerosols were 5.4 ± 0.2 in Xi'an and 5.7 ± 0.2 in Beijing (Huang et al., 2020).

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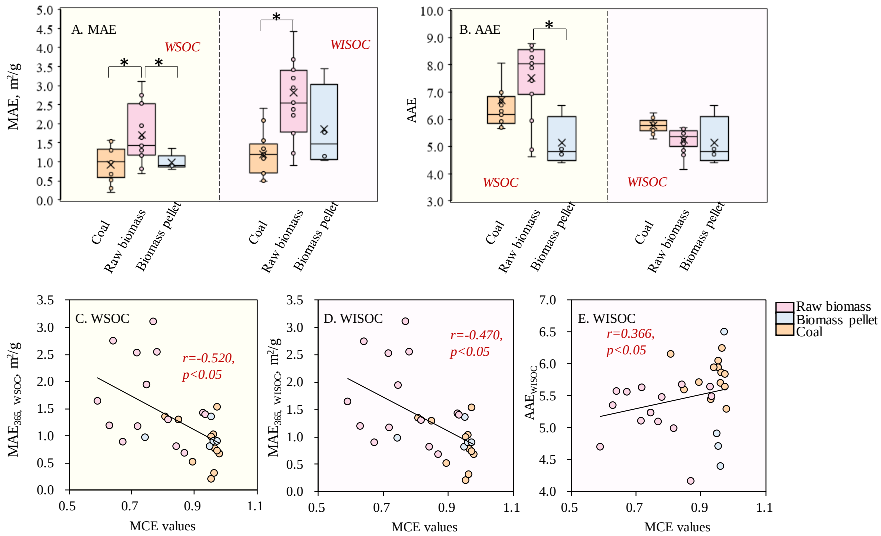

209 **Fig. 1** MAE values at λ=365 nm (A) and AAE values (B) from the source samples (* represents
210 p<0.05); Correlation between the MCE values with $MAE_{365, WSOC}$ values (C), $MAE_{365, WISOC}$ values
211 (D), and AAE_{WISOC} values (E).

212 3.2 Molecular characteristics of WSOC and WISOC

213 The ESI-FT-ICR mass spectra of WSOC and WISOC samples are presented in Fig. 2.
214 Thousands of peaks were identified in the m/z range of 150-800, indicating a complex chemical
215 composition of aerosols from residential sources. Formulas detected in the raw biomass burning
216 aerosols were significantly higher than those in biomass pellet and coal smokes (Fig. S3), which
217 indicated a higher chemical complexity of raw biomass emissions. In addition, the combustion of
218 pine wood in the improved stove generated less compounds, which was 93% peaks of that in the
219 traditional stove (Table S2). The likely less complexity might be due to higher combustion
220 efficiencies and temperature in the improved stove. Generally, higher levels of organic aerosols
221 mass would be emitted during less efficient fuel burning, resulting from prolonged smoldering or
222 incomplete burning (Holder et al., 2016). Our results suggested that corresponding higher chemical

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complexity were also produced during the incomplete combustion in the traditional stove. The most intense ion peaks were distributed in the 200-500 m/z for WSOC, accounting for 58-86% of the total intensity. Similar results were also found in residential coal combustion (Song et al., 2019), biomass burning (Song et al., 2018), and ambient aerosols (Wozniak et al., 2008).

The mass spectra of WISOC are different from the WSOC, especially in aerosol emitted from coal combustion (Fig. 2). WISOC contained more molecules with larger m/z values of 600-800 in range, which indicated that WISOC extract had more compounds with higher MW than the WSOC extract. According to the molecular formulas and the intensity of each negative ion, the average molecular formulas for the WSOC were obtained with C atom from 20 to 24, H (21-29), N (0.32-0.75), O (5.6-7.0), and S (0.28-0.51) in the WSOC extract. All aerosols from biomass burning, either raw or pelletized ones, had higher relative O atom contents than coal smokes, indicating a higher oxidation degree of biomass emissions. For the WISOC, the average molecular formulas were assigned with 27-33 C, 26-35 H, 0.67-1.2 N, 6.6-11 O, and 0.34-0.92 S. The coal combustion derived aerosols had more C, N, and S atoms, but less H atom, compared with raw biomass. The combustion of biomass pellet also assigned with relative higher S elements. In addition, the WISOC fraction had a higher relative atom content than corresponding formulas of WSOC from the same source aerosol samples. These results indicated that in addition to the fuel type, extraction solvent also had important impact on the elemental composition of extractable BrC.

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Fig. 2 Negative ESI FT-ICR mass spectra of WSOC (A-G) and WISOC (A'-G') from the seven aerosol samples. Different formula groups were color-coded. The pie charts showed the relative intensities of different formula groups.

Molecular formulas identified by the FT-ICR-MS can be classified into 4 groups according to the elemental composition, including CHO (containing only C, H, O), CHON (hereafter similarly), CHOS, and CHONS. CHO was the most abundant group in the WSOC. The CHO group contributed 51-67% to the total intensity in aerosols from raw biomass burning, which were significantly higher than those from biomass pellets (29-39%) and coal smokes (30-40%). The CHO compounds with oxygen-containing functional groups (e.g., hydroxyl, carbonyl, carboxyl, or esters) have been widely identified in both ambient aerosols (Jiang et al., 2021; Mo et al., 2022) and some source sample (Tang et al., 2020). These compounds contributed a broad range of proportions, from 43%

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to 69% in residential biomass burning smokes (Tang et al., 2020), 9.7-48% in coal smokes (Song et al., 2019), and 20-39% in ambient aerosols (He et al., 2023) for the WSOC extract, which were comparable to ours. CHON compounds were also an important component in the aerosols, accounting for 29-36% in coal smokes, which were significantly higher than biomass burning smokes of 11-28%. One previous study reported that CHON species were more abundant in biomass burning smoke rather than the coal combustion ones (Song et al., 2018). This high fraction of CHON compounds in coal smokes might be caused by higher nitrogen content of coals as seen in Table S1. A strongly significantly positive correlation was found between the fuel nitrogen content and CHON species percentage (r=0.936, p<0.05) (Fig. 3). Such dependence was also found in the emission factors of NO_X (NOx EFs) on fuel nitrogen content in our result (Fig. S4), as well as NOx, HCN, and NH_3 emissions reported by published literatures (Hansson et al., 2004)-. Sulfur-containing compounds (SOCs; including CHOS and CHONS) abundance was lower than CHO and CHON group, accounting for only 22-42% (13–30% for CHOS and 7.9–28% for CHONS, respectively). The fractions of SOCs in the aerosols from coal combustion (25-42%) and biomass pellet burning (~42%) were comparable, but significantly higher than those from raw biomass (22-31%). The abundance of SOCs was not statistically correlated with fuel S content in the present study for pooled data. However, when fuel subgroups were considered, fuels (coal or raw biomass) with higher sulfur content had higher SOC levels. Also, higher SOCs emission was found for pine wood combusted in improved stove which have higher combustion efficiency than that in traditional stove. These results suggesting that except for fuel sulfur content, the fuel type and combustion efficiency would also influence the SOC emissions.

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In the WISOC, intensities of these four groups among different source samples were different from that in the WSOC. The CHO group accounted for 27-45% in raw biomass burning aerosols, 22-24% in biomass pellet smokes, and 13-22% in coal smokes. On the contrary, the SOCs abundance was significantly higher in WISOC, especially for the coals, accounting for 58% for HVB, and 52% for MVB. Significantly Positive correlation between the MCE values and SOCs abundance in the WISOC extract was found (r=0.750, p<0.05) (Fig. 3), while no clear association between fuel sulfur content and SOCs emissions observed in the WISOC. Combining the result from the WSOC extract, strong dependence of SOCs emissions on the combustion conditions were expected, while the fuel sulfur content had slight influence. Notably, the SOC abundance in aerosols from coal combustion was greatly higher than that in ambient aerosols (Lin et al., 2012), indicating that residential non-desulfurized coal combustion might be an important emitter of SOC in atmospheric samples. Thus, the CHON group emissions were determined mainly by the fuel nitrogen content, while SOCs emissions were strongly related to the combustion conditions (e.g., flaming phase). It should be noted that the results of our analysis based on the current data without isotopic internal standard used were semi-quantitative, there are uncertainties that must be addressed.

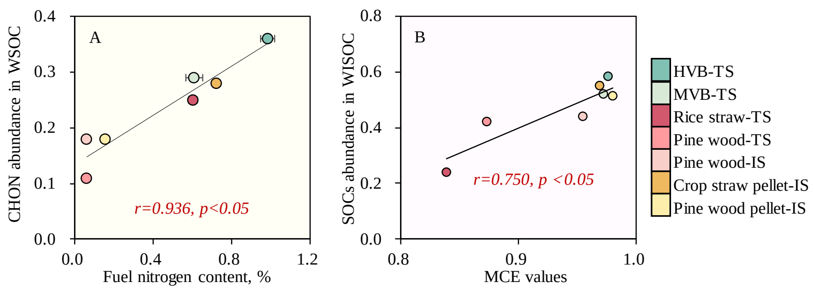

Fig. 3 Correlation between fuel nitrogen contents and abundances of CHON in WSOC (A), and the correlation between MCE values and the abundances of SOCs in WISOC (B).

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3.3 Detailed CHO/CHON/CHOS/CHONS group differences across fuel types

Van Krevelen (VK) diagrams which can provide a visual interpretation of complex mass spectra can qualitatively identified chemical composition profiles in mixtures(Lv et al., 2016).The classification criteria of the VK diagram are provided in Table S3 (Patriarca et al., 2018; Tang et al., 2020). Fig. S5 and S6 show the VK diagrams of WSOC and WISOC. In both WSOC and WSOC extract, the carboxylic-rich alicyclic molecules (CRAMS-like) was the most abundant component, contributing to 53-69% in the WSOC extract and 37-56% in the WISOC extract, respectively. The condensed aromatics were also an important component in source samples, accounting for 7.3-13% in the WSOC, and for a higher proportion of 8.6-44% in the WISOC. This observation could be attributed to the hydrophobic property of condensed aromatic hydrocarbons, leading to a lower proportion in the highly polar WSOC. Among the identified formulas, 7.0-13% of total intensity in the WSOC and 3.6-17% in the WISOC were the aliphatic/peptides like compounds. Such fractions were comparable to unsaturated hydrocarbons with percentages of 3.9-15% in the WSOC and 2.0-11% in the WISOC. The compounds including lipids-like species and highly oxygenated compounds (HOC) were in a relatively lower abundance, with less than 10% each in the source samples. The different fuels showed varied chemical composition characteristics. Coal combustion aerosols had lower H/C ratios than those in biomass burning aerosols, indicating higher unsaturated degrees (Table S2). As indicated by the VK diagrams, the coal combustion produced a notable number of condensed aromatics, contributing to 27%-44% in the WISOC, which was significantly higher than that of 8.6-21% in the biomass burning emissions. The modified aromaticity index ($AI_{mod,w}$) which is a measure of aromatic and condensed aromatic structure fractions and DBE values which is used as a measure of the unsaturated level in a molecule were all higher for coal emissions compared to the biomass emissions.

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Distinct compound profiles being identified by the VK diagram classification criteria are consistent with discrepancies in the four (CHO/CHON/CHOS/CHONS) groups. For the CHO group, the most intense compounds were CARMs compounds with fractions of 69-84% in the WSOC extract and higher fractions of 51-80% in the WISOC extract. It was observed that raw biomass would emit slightly more CRAMs (76-84% and 61-80% in the WISOC) than coal (69-73% in the WSOC and 62-69% in the WISOC) and biomass pellet (70-75% in the WSOC and 51-56% in the WISOC) combustion. The condensed aromatic compound was also a crucial component, accounting for 13-20% in the WSOC and 19-27% in the WISOC of coal emissions. These fractions were significantly higher than those found in raw biomass (4.5-10% in the WSOC, and 7.9-10% in the WISOC) and biomass pellet (3.8-5.4% in the WSOC, and 11% in the WISOC) (Fig. 4). The other components accounted for a small (less than 10% each) of the total CHO intensity.

It was reported that the CHON compounds with O/N≥3 might be the organonitrates candidate and nitro-substituted compounds, attributing to the allocation of one nitro (NO_2) or nitrooxy (ONO_2) group (Bianco et al., 2018). In this study, the relative content of $CHON_{O/N\geq3}$ compounds (with respect to the overall CHON) in the biomass (raw and pellet ones) ranged between 71-82% and 85-91% for the WSOC and WISOC, which is distinctly lower than those found in coal smokes (86-90% for the WSOC, and 86-95% for the WISOC) (Table S4). Moreover, the $AI_{mod,w}$ values for CHON compounds from coal combustion were higher than the biomass smokes for both WSOC and WISOC, 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 biomass fuels. Coal combustion emissions had more intense condensed aromatic compounds with percentage of 45-50% for the CHON group, which were significantly higher than those from raw biomass (4.5-37%) and biomass pellet burning (14-30%). This result confirmed the conclusion that the CHON compounds produced from the combustion of coals were characterized

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by a relatively high aromaticity and a low degree of oxidation.

The O-rich CHOS fraction (O/S≥4) accounted for 42−71% (concerning the overall CHON group) in the WSOC and 45-95% in the WISOC. O-rich CHOS fraction (O/S≥4) content from coal (66-70% in the WSOC, and 78-98% in the WISOC) and biomass pellet (67-71% in the WSOC, 76-87% in the WISOC) were relatively higher than the raw biomass smoke (42-56% in the WSOC, and 32-57% in the WISOC), suggesting that most of the CHOS compounds in coal and pellet smoke can be potentially assigned with more bearing sulfate (-OSO_3H) or sulfonate (-SO_3) groups. Different from CHO and CHON group, it was found that CHOS group in the biomass burning aerosols had much more intense condensed aromatic structure with percentage of 14-33% in the WSOC and 2.5-19% in the WISOC, especially for raw biomass (WSOC: 22-33%, WISOC:8.5-19%), than coal combustion (WSOC: 4.9-7.0%, WISOC: 2.5-7.0%). For CHOS group in the WISOC extract, the unsaturated hydrocarbons were also an important component, accounting for 12-29% in raw biomass burning emissions, which were significantly higher than those in biomass pellet (6.9-11%) and coal (1.5-13%). These results indicated biomass burning emissions were characterized with higher unsaturation level and aromaticity for the CHOS group than coal combustion.

Nearly 34-85% of CHONS formulas have a large number of O atoms (≥7), indicating the existence of -NO_3 group (Table S4). These CHONS compounds are probably nitrooxy-organosulfates (Song et al., 2019).The remaining compounds (15-66%) of CHONS group had less than 7 atoms, implying that large amounts of CHONS compounds were assigned with reduced N (e.g., amide and nitrile, and heterocyclic aromatics). The condensed aromatic compounds identified by the VK diagram in the WISOC from coal combustion accounted for 22-64%, which were relatively higher than those from biomass burning (14-31%), indicating a higher degree of aromaticity. This was consistent with the difference observed in the $AI_{mod,w}$ values as seen in Table

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S2. The $AI_{mod,w}$ of WISOC in coal emissions were 0.38 for HVB and 0.60 for MVB, and the values were higher than the raw biomass (0.32-0.38) and biomass pellet (0.35-0.36), confirming a higher aromatic compounds content of coal smoke sample than biomass for CHONS group.

Therefore, the CHO, CHON, and CHONS groups generated from coal combustion were characterized by high unsaturated level with more aromatic species, while CHOS groups had higher aromaticity degree in biomass smoke aerosols. Aromatic compounds might be the strong BrC chromophores contributing to light absorption (Song et al., 2019). The difference in MAE between coal and biomass emissions and association with the chemical components will be discussed in detail in the section 3.5.

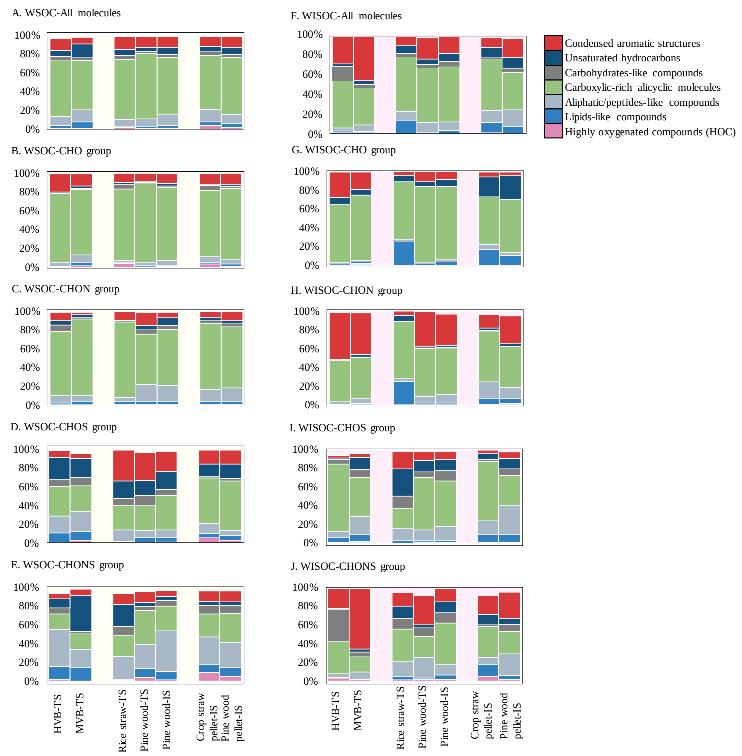

Fig. 4 Each component abundance identified by VK diagram of WSOC (A: all molecules, B: CHO group, C: CHON group, D: CHOS group, E: CHONS group) and WISOC (F: all molecules, G: CHO group, H: CHON group, I: CHOS group, J: CHONS group), the classification criteria was provided in the Table S3.

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3.4 Likely unique molecules of biomass and coal combustion

The unique molecules may be inferred from the Venn diagram of formulas as shown in Fig. S7. Among the observed compounds, 3039 and 1624 unique molecular formulas were detected in the combustion of rice straw and pine wood in the traditional stove. These were significantly more than the unique formulas detected in biomass pellet-improve stove (638-696) and coal-traditional stove (570-734) in the WSOC fractions, suggesting a notable difference between the emissions from raw biomass and coal, even when using the same stove. Interestingly, fewer unique peaks were observed for pine wood-improved stoves (533), indicating that using an improved stove for raw biomass could narrow the difference between coal and biomass emissions. The similar trend was also found in the WISOC fractions (Fig. S7). The CHONS group accounted for a significant portion of unique formulas in source samples, particularly in coal smokes, representing 51-52% in WSOC and 51-69% in WISOC extract. The important role of CHONS group for unique emissions from coal combustion was also noted by Tang et al., (2020), who reported that CHO and CHON were the main component of unique molecular formulas of raw biomass burning emissions among the raw biomass burning, coal combustion and vehicle emissions, representing 88%-93%. This fraction was higher than our result of 33-77% in raw biomass and only 26-27% in biomass pellet. The distribution of the unique molecules further indicated substantial discrepancies among the fuels. Unique molecules in coal combustion derived aerosols were located in the region with lower H/C and O/C value compared with all other samples (Fig. 5) in both WSOC and WISOC extract, indicating a higher degree of unsaturation and lower level of oxidation. For example, it was observed that specific emissions from coal combustion were mainly composed by condensed aromatics (32-59%), followed by CRAMs compounds (23-39%) in WISOC extract. However, only 4.3-9.7% condensed aromatics of the total unique emissions were observed for biomass burning, with CRAMs being the main component (39-65%). As for different groups of CHO/CHON/ CHONS, the condensed aromatic compound contents

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for all three groups in coal smoke aerosol (unique detected ones) were relatively higher than biomass. While CHOS group showed different trend that condensed aromatic compound contents of biomass smokes (unique detected ones) were relatively higher than coal smokes in WSOC extract and comparable to coal smokes in WISOC extract. This finding highlighted the CHOS group importance in distinguishing the aerosols from the combustion of coals or biomass, helping conduct the source apportionment of aerosols. Additionally, compared with the pine wood-improved stove emissions, most unique molecules in aerosol from pine wood-traditional stove combustion were in the region with lower H/C and O/C ratios (Fig. 5), which were identified mainly as CRAMs compounds. While the emissions from improved stove were distributed in a wider range with less CRAMs compounds and more aliphatic/peptides-like compounds observed. Unique molecules from biomass pellet combusted in improved stove distributed in the upper region of the VK diagram with higher H/C values in WISOC extract, which indicated a lower unsaturated degree (Fig. S8).

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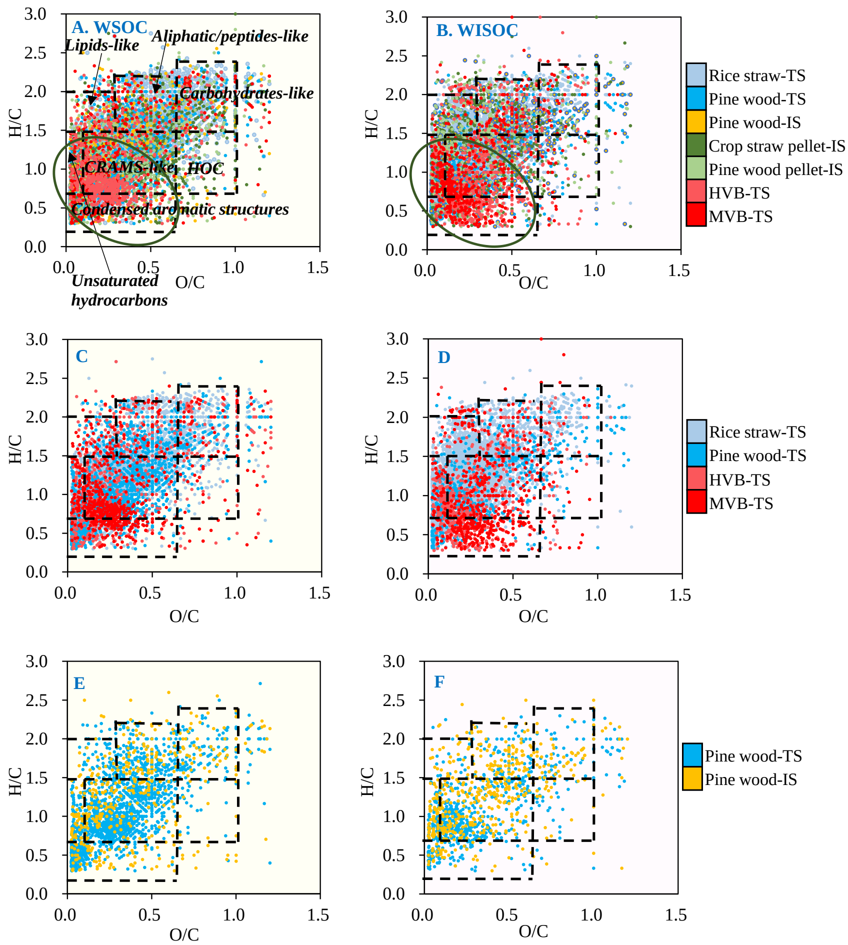

Fig. 5 Van Krevelen diagrams of WSOC (left) and WISOC (right) from the source samples. Different color indicates unique formulas detected in each sample of solid fuel combustion.

A total of 484 molecular formulas were detected simultaneously in the seven aerosol samples in the WSOC extract and 306 in the WISOC extract. Among these commonly detected molecules, most of which were CHO compounds with the molecular numbers accounting for 60% and 73% in the WSOC and WISOC, respectively. CHON accounted for 31% of WSOC and 19% of WISOC, while SOCs only occupied about 10%. As seen in the Fig. S9, these CHO compounds were mainly composed of CRAMs-like compounds, and also several lipids-like and aliphatic/peptides-like compounds. Moreover, these compounds were relatively small molecular compound assigned with 8-28 C atom and 2-12 O atom with DBE values of 2-17 for the WSOC extract. The relatively more C atom assigned with larger DBE values was observed for the CHO compounds in WISOC, which could be partially explained by that the overall CHO compounds in the WISOC extract had larger MW values with a high degree of unsaturation. In total, the CHON compounds were also CRAMs-like compounds, and almost none compounds were expected to be aromatics. CHOS and CHONS species had much fewer formulas, especially for CHONS, only accounting for 1.0% in the commonly detected molecules in the WISOC. The unsaturated levels of commonly detected molecules in all seven source samples were relatively low. For example, the condensed aromatic compounds accounted for 6.5-9.3% and 3.3-4.1% of the total intensity for coal smoke and biomass smoke in the WSOC, respectively, as well as 0.38-8.3% and 18-21% in the WISOC extract. Different from the CHO, CHON, and CHONS group, high percentages of condensed aromatic compounds were found in CHOS group (commonly detected ones) from raw biomass burning aerosols with range of 6.6-51% in the WSOC and 12-46% in the WISOC extract. These fractions were significantly higher than those from coal smokes of 4.1-4.9% in the WSOC and 8.8-25% in the WISOC extract. Combining the finding that CHOS group in biomass smokes had a higher aromaticity degree in both WSOC and WISOC extract. However, the unique molecules in WISOC extract did not follow this trend. It was thus speculated that the higher aromaticity degree of CHOS group in biomass smokes was attributed to the intensity variation of these simultaneously detected compounds, rather than the unique emission from special source for the WISOC extract.

To explore the potential influence of fuel properties and combustion conditions on chemical composition, the major factors such as fuel moisture, V_{daf}, and parameters reflecting combustion conditions including MCE, EC/OC ratios were assessed. The liner correlation analysis was applied to estimate the effect of these factors on each molecular intensity (commonly detected ones)

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(Fig.S10 and S11). The aliphatic compounds (including lipids like, aliphatic/peptides like and carbohydrates like compounds) were negatively correlated with the fuel moisture and positively correlated with V_{daf} and EC/OC ratios. Fuel moisture has been recognized as an important factor influencing pollutant formation, but the influence is usually very complicated. The observed relationship between fuel water content and pollutant EFs varies largely among studies, which may be attributed to factors such as different water contents, pollutant types, and interactions among other influencing factors. Fuels with high moisture levels may have high emissions, as extra energy is needed to vaporize water during the burning process; however, a decrease in combustion temperatures under very high-water content conditions may slow the pollutant formation rate and consequently lower emissions. Higher EC/OC ratios and larger MCE values tend to be associated with stronger flaming conditions. The results suggested that the aliphatic compounds were apt to be produced on the period of the flaming phase with higher combustion temperature. This result could partially explain that aliphatic/peptides like compounds would be apt to be produced in the improved stove rather than the traditional stove. In comparison, the emissions of CRAMs-like compounds which is the most abundant species were decreased with the increased MCE and EC/OC values, indicating that CARMs-like compounds were generated under smoking phase. No significant correlations of aromatics, unsaturated hydrocarbons, and HOCs were observed with these parameters, resulting from their small proportion in commonly detected molecules. It is worth noting that there may be significant differences, even for the same fuel, in chemical composition depending on other factors such as stove type and combustion conditions. The interactions among these factors making it difficult assessing their influence. It was found that only around 50% identified molecules were overlapped emissions for pine wood combusted in traditional stove and in improved stove, suggesting the importance of stove used. Fewer fraction of 25-30% molecules were observed compared the pine wood emissions with coals combusted in the same stove, which

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suggested that the influence of varied fuels on chemical composition could surpass the differences caused by different stoves. Our previous studies have revealed that fuel type was the most important factor influencing on the MAE values (Zhang et al., 2021b) and BrC EFs (Zhang et al., 2021a). The present study highlighted the dominant effect of fuel type on the chemical composition of soluble OC, providing a theoretical basis for source appointment based on molecular composition. Moreover, the combustion conditions would have significant effect on the molecular intensity, resulting in differences in MAE eventually as indicated in the section 3.1.

3.5 The correlation of light absorption properties with molecular compositions

Here we specifically look into the variability in optical characteristics among the different fuels attributed to its chemical compositions. No significant correlations were observed between the AAE values of soluble OC and the molecular composition, indicating that AAE could be influenced by many factors. The MAE may be influenced by the degree of oxidation and unsaturation degree (Mo et al., 2017) (Tang et al., 2020), however, there was no significant correlation found between the MAE values and O/C values in the present source samples, implying that the BrC light absorption ability might not be directly affected by its oxidation degree.

The $MAE_{365,\ WSOC}$ values were significantly positively correlated with the DBE values ($r=0.786$, $p<0.05$) and the MW values ($r=0.750$, $p<0.05$) (Fig. S12), indicating that unsaturation and MW played a crucial role in the light absorption capability of the source samples. In the above discussion, we have noticed that CHOS group in biomass was characterized by higher degree of aromaticity than coal smoke aerosol, while CHO, CHON, and CHONS group have a higher aromatic degree in the coal emissions. A significantly positive correlation ($r=0.714$, $p<0.05$) was observed between $MAE_{365,\ WSOC}$ values and the condensed aromatics percentages from the CHOS group (Fig. 6), indicating that aromatics in CHOS group contributed to the high light absorption ability of

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biomass smokes.

For the WISOC extract, no significant correlation was found between the $MAE_{365, WISOC}$ values with MW or DBE values, which might be explained by much different chemical composition for insoluble compounds compared with soluble parts Although the coal combustion emitted much more aromatic compounds with higher DBE values for the WISOC, the MAE values were not significantly higher. The significantly positive correlation (r=0.929, $p<0.05$) between $MAE_{365, WISOC}$ values and the CHOS condensed aromatics percentages confirmed the importance of CHOS aromatics in determining the light absorption capability from source samples. As mentioned in the Section 3.4, higher aromaticity degree of CHOS group in biomass smokes was largely due to the intensity variation of these commonly detected compounds in all source samples. The further analysis revealed that $MAE_{365, WISOC}$ values were positively correlated (r=0.750, $p<0.05$) with the CHOS condensed aromatics fractions which were the fraction simultaneously detected in all samples. These results indicated that light absorption capability of source aerosols may be due to the higher abundance of some CHOS aromatic compounds commonly emitted from both coal and biomass, rather than the unique tracers.

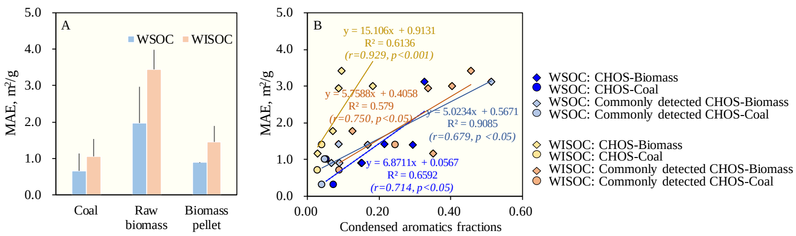

Fig. 6 MAE values at λ=365 nm (A) and correlations between condensed aromatics fractions in CHOS and in commonly detected CHOS with MAE values (B) from the source samples

4. Conclusion and implication

The $MAE_{365, WSOC}$ ranged from 0.21 to 3.1 m^2/g with an average of 1.3±0.7 m^2/g. The $MAE_{365, WISOC}$ was found to be higher with an average of 2.0±1.3 m^2/g. There were significant differences

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(p<0.05) observed among the different fuels for both $MAE_{365,\ WSOC}$ and $MAE_{365,\ WISOC}$, as raw biomass burning combustion had significantly higher values than the coal combustion. The AAE_{WSOC} ranged from 3.8 to 11 with an average of 6.9±1.5. The AAE_{WISOC} were slightly lower than AAE_{WSOC}, which ranged from 4.2 to 6.5 with an average of 5.5±0.5. Thousands of peaks were identified in the m/z range of 150-800, indicating a complex chemical composition of aerosols from residential sources. CHO group was the most abundant component in the WSOC extracts and the contribution of CHO compounds to the total intensity in aerosols from raw biomass burning was significantly higher than those from biomass pellets and coal smokes. On the other hand, WISOC extract contained more SOCs, especially in the coal combustion aerosol. Notably, CHON compounds were more abundant in the coal combustion emissions, which was due to the higher fuel N content of coals (r=0.936, p<0.05). The SOCs emissions were more predominant in flaming phases, as positive correlation between SOCs abundance with the MCE values (r=0.750, p<0.05).The CHO, CHON, and CHONS groups generated from coal combustion were characterized by high unsaturated level with more aromatic species, while CHOS groups had higher aromaticity degree in biomass smoke aerosols. It was found that MAE values were positively correlated with the CHOS condensed aromatics proportion for both WSOC (r=0.714, p<0.05) and WISOC extract (r=0.929, p<0.001).These results indicated that higher CHOS condense aromatics abundance in biomass burning aerosols could partly explain the higher MAE values of raw biomass smokes. The further analysis showed positive correlation of MAE with the CHOS condensed aromatics fractions which were the fraction simultaneously detected in all samples. These results indicated that light absorption capability of source aerosols may be due to the higher abundance of some CHOS aromatic compounds commonly emitted from both coal and biomass burning, rather than the unique tracers. The unique formulas of coal combustion aerosols were in the lower H/C and O/C regions with higher unsaturated compounds in the VK diagram. This work is potentially applicable to the

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source appointment based on the molecular characteristics and to future studies developing more scientific control measures by focusing on one major component (e.g., CHOS condensed aromatics) of light absorption aerosols.

There are still some questions that need to be investigated in the future study. First, the study on BrC composition in this research used dissolved OC as a substitute. However, this substitute cannot fully represent BrC emissions. Both WSOC and WISOC contain some non-light-absorbing component, and the proportion of these components is unknown, making it difficult to measure the representativeness of extractable OC for BrC. Additionally, the lack of study about the emissions characteristics under controlled combustion conditions limits the obtained results. The controlled experiment including flaming or smoldering burns, air flow, and combustion temperature are needed in the future work. Third, fresh burning-derived OC released into the atmosphere can undergo various aging reactions such as photochemical degradation. These reactions can significantly alter the light absorptivity and chemical properties of BrC components. It is essential to consider the optical properties and lifetimes of organic compounds emitted from solid fuel combustion in climate models.

Data availability.

Data are available by contacting the corresponding authors

Supplement

The following information is in the appendix and available via the Internet:

Data processing in the ESI FT-ICR MS; fuel properties of coal and biomass fuels tested; number of formulas in each group, values of elemental ratios, MW, and DBE values in the WSOC and WISCO for each source type; Stoichiometric ranges of VK classes; Correlation between fuel N and emission factors of NOx; the VK diagrams of WSOC and WISOC for different source samples; and correlations between the VK plots of WSOC/WISOC and fuel properties or combustion conditions.

Author contributions

LZ, GS, and ST designed the experiment. LZ and JL prepared the filters used. LZ, YL, XL and ZL conducted the sample collection. LZ and JL performed the data analysis. LZ wrote the paper. GS, and ST reviewed and commented on the paper.

Competing interests

The authors declare that they have no conflict of interest.

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