Molecular compositions and optical properties of dissolved brown carbon in smoke particles illuminated by excitation-emission matrix spectroscopy and Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) analysis

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Abstract: We investigated the fluorescence and chemical-structural characteristics of dissolved brown carbon (BrC) in smoke particulates emitted from the combustion of biomass and fossil fuels (coal and vehicle exhaust) by excitation-emission matrix (EEM) spectroscopy and Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) coupled with electrospray ionization (ESI). Six components were resolved by parallel factor analysis (PARAFAC) of the water-soluble and methanol-soluble organic carbon (MSOC) fractions, respectively. These fluorescent components varied among sources. Combined with FT-ICR MS ion groups, we found that the fluorescent components agreed well with the functional groups, particularly with nitrogen (N)- and sulfur (S)-containing groups. Among the six PARAFAC components (P1–6) retrieved from the water-soluble organic carbon (WSOC) fraction, except for the P3 component, the other components exhibited different values among the three types of emission sources tested. Vehicle exhaust was characterized by high P1 and P6 components, which are mainly associated with aromatic organosulfate compounds, and a high P5 component, mainly associated with sulfonates; coal combustion was characterized by a high P4 component, which is associated with nitrooxy-organosulfate (nitrooxy-OS) compounds; and biomass burning was characterized by the P2 component. Similar results were observed in the case of the MSOC fraction. This study reveals the source contribution and possible structures of previously unclear excitation-emission matrix (EEM) fluorescent components in combustion-derived aerosols. These are the first findings of this type and are potentially applicable to further studies on EEM-based source apportionment of dissolved BrC in aerosols.
1 Introduction

Carbonaceous aerosols play an important role in the Earth’s radiative balance. One such aerosol, black carbon (BC), absorbs significant amounts of light and exerts a warming effect, while organic carbon (OC) was initially thought to only scatter solar radiation (Wong et al., 2017; Mo et al., 2017; Saleh et al., 2014). However, there are certain types of OC that absorb radiation efficiently in the near ultraviolet (UV) (300–400 nm) and UV-visible (UV-Vis) ranges, which are called brown carbon (BrC) and are able to positively shift the net direct radiation forcing (DRF) (Saleh et al., 2014; Laskin et al., 2015; Chen and Bond, 2009; Kirchstetter and Thatcher, 2012). According to a simulation model, the inclusion of BrC may enhance total aerosol absorption by 7–19% (Feng et al., 2013). BrC mainly originates from emissions from biomass burning and fossil fuel combustion, and the formation of secondary organic aerosol (SOA) (Zhu et al., 2018; Laskin et al., 2015). Among the various sources listed above, primary emissions contributed significantly to BrC absorption (Fan et al., 2012; Yan et al., 2015; Zhang et al., 2011). Recently, many studies have investigated the chemical and optical properties of BrC in smoke particles emitted from biomass burning, coal combustion in a control laboratory chamber (Park and Yu, 2016; Fan et al., 2016; Chen and Bond, 2009) and emissions characteristic of vehicle emissions (Dai et al., 2015). However, most studies mainly focused on light absorption of BrC; little structural information is available.

Excitation-emission matrix (EEM) spectroscopy has been widely applied to identify the sources and chemical nature of chromophoric dissolved organic matter (CDOM) in aquatic environments since the 1990s (Shimabuku et al., 2017; Wells et al., 2017; Bhattacharya and Osburn, 2017; Coble, 1996), while few studies have focused on the fluorescence properties of chromophores in atmospheric environments. Recently, many studies have suggested that the optical properties of chromophoric water-soluble organic carbon (WSOC) in the atmosphere was similar to CDOM in aquatic environments (Qin et al., 2018; Fu et al., 2015), and this could be extended to atmospheric research. Fluorescence is a radiative process that occurs between two
energy levels of the same multiplicity (Andrade-Eiroa et al., 2013). Compounds with rigid planar structures and highly conjugated systems have intrinsic fluorescence emission characteristics, such as aromatic acids, phenols, nitroaromatics, polycyclic aromatic hydrocarbons (PAHs), quinones, and so on, which are important BrC chromophores (Lin et al., 2018; Zhang et al., 2013). Furthermore, Laskin et al. (Laskin et al., 2015) believed that fluorescence is sensitive to the molecular (or supramolecular) identity of BrC compounds and anticipated that fluorescence-based methods will become increasingly important in the study of BrC. Fluorescence spectra, which are considered a “fingerprinting” tool, have been applied to organic aerosols (Fu et al., 2015; Chen et al., 2016b). Chen et al. (Chen et al., 2016b) observed that the fluorescence spectra of water-soluble organic matter from urban, forest, and marine aerosols varied depending on the sampling site and period, and were affected by oxidative and functional groups. Lee et al. (Lee et al., 2013) reported that SOA derived from the oxidation of limonene and decene with O3 and OH presented different fluorescence spectra. The biggest challenge when analyzing chromophoric BrC using fluorescence spectra, however, is the lack of a classification system for fluorescence spectra, to distinguish chromophores from the majority of nonabsorbing constituents and to determine the chemical structures of the chromophores. The combination of Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) coupled with electrospray ionization (ESI) and EEM is a powerful platform for characterizing BrC chromophores, and is expected to enable us to deduce the molecular compositions of these chromophores. FT-ICR MS has been successfully used to characterize organic aerosol (Jiang et al., 2016; Song et al., 2018; Mo et al., 2018), cloud water (Zhao et al., 2013), and natural organic matter (Sleighter et al., 2012; Feng et al., 2016). The ultrahigh resolution, accuracy of mass measurements, and high sensitivity make this technique suitable for studying complex mixtures at the molecular level, and for identifying the chemical compositions of the substances being studied with a high degree of confidence (Feng et al., 2016).

Residential coal combustion and biomass burning are very important anthropogenic sources of air pollutants, especially fine particulate matter (PM2.5), in
Concerns about the environmental and health effects of vehicle emissions have existed for decades (Dai et al., 2015). The characteristics of BrC from these origins may differ to those of BrC from other sources. To obtain a comprehensive understanding of BrC originating from different sources, we investigated the solvent extractions of organic compounds with different polarities from the smoke particles of simulated combustion emissions from biomass fuel, coal, and vehicles, and characterized their optical properties in terms of UV-Vis absorption and excitation-emission matrix (EEM) spectra. We employed FT-ICR MS coupled with ESI to investigate the molecular compositions of the fluorescent components identified by parallel factor analysis (PARAFAC). We also aimed to identify the possible chemical structures of these chromophores and create a source library of BrC chromophores for applications to atmospheric BrC apportionment based on fluorescence technology.

2 Experimental methods

2.1 Sample collection and preparation

The smoke particle were collected by the instrument coupled with dilution channel which was designed to simulate fire emissions representative of “real-world” open biomass burning and household coal combustion activities (Figure S1). In present study, a total of 27 biomass burning samples (IDs: 1-27) were collected at Xishuangbanna city, Yunnan Provence, from May 20th to June 3th, 2016 and the detailed sampling process was described in our previous article (Cui et al., 2018). In short, raw fuels (rough 20×3×2 cm³) were air-dried for several days, and ignited in a stainless steel bowl, and then the rising smoke was collected through a dilution system. The sampling system mainly consisted of a dilution tunnel, a residence time chamber, three particulate matter (PM) samplers, and so on. Every biomass about 1-2 kg fuels was burned three times, and each combustion process lasted for 20 minutes. The collection of smoke particle started when fuel ignited, and end until the concentration of CO₂ down to atmosphere CO₂ level. Dilution ratios of each experimental process
were calculated using the CO\textsubscript{2} concentrations before and after dilution. The collection flow rate and average dilution ratio were 180 L/min and 2.1, respectively. And the other 6 biomass burning samples (IDs: 28-33) were collected at Guangzhou city, Guangdong Province.

The smoke particle of coal combustion (IDs: 34-50) were collected as same as that of biomass burning, but used a stove, at Guangzhou city, Guangdong province, from Nov 18th, 2017 to Jan 23th, 2018. The tested stove is technically improved stoves (named Jin-Yin stove). Due to the difficult of ignition of coal, we used smokeless charcoal to ignite one-third (about 300 g) of the raw-coal chunk (2-5 cm in size) in stove, removed the charcoal after ignition, and then added the remaining raw-coal chunk (about 700 g) to start to collect the smoke particle. Every coal about 1 kg fuels was burned three times, and each combustion process lasted for about 40-150 minutes. The collection flow rate and average dilution ratio were 150 L/min and 1.5, respectively. Additional, a modified combustion efficiency (MCE) was calculated to characterize the relative amount of smoldering and flaming combustion phase (Lin et al., 2016; Cui et al., 2018). The average MCE values were 0.73 ± 0.08 for coal combustion, but unavailable for biomass burning because the CO sensor did not work in the field work which was mentioned in our previous paper (Cui et al., 2018).

Eight tunnel samples (IDs: 51-58) were collected at Siping Tunnel from Nov 1th to 2th, 2017 and Xiaoyangshan Tunnel from Dec 1th to 2 th, 2017, in Shanghai city, as well as two vehicle exhaust samples (IDs: 59-60) were collected from truck. The filters were wrapped in aluminum foil and pre-baked at 450 °C for 5 hours before sampling, and stored at -20 °C after sampling. There were a total of 60 total suspended particulate matter (TSP) samples on source emission in the current experiment, and blank samples which were collected at different times and locations were used for correcting filter samples.

WSOC for UV-Vis absorption and EEM analysis was extracted with purified water (resistivity of >18.2Ω) via ultra-sonication of quartz filter punches for 30 minutes. After the extraction, we obtained the methanol-soluble organic carbon (MSOC) constituent by freeze drying the water-extracted filter and performing
 ultrasonic-extraction with methanol (HPLC grade) in the same manner. Note that the
MSOC fraction of the methanol extract in our current study are not necessarily similar
to those of the same names in other studies. All of the extracts were filtered through a
0.22 um polytetrafluoroethylene membrane into amber colored glass vials to remove
the insoluble material.

2.2 Carbon analysis
We measured both OC and elemental carbon (EC) using an aerosol carbon analyzer
(Sunset Laboratory, Inc., USA), following the NIOSH thermal-optical transmittance
(TOT) standard method (Mo et al., 2017), and the emission factors (EFs) of PM, OC
and EC were calculated and detail information was presented in supplement. We also
analyzed the elemental compositions of biomass (C, H, O, and N) and coal (C, H, O,
N, and S) using an elemental analyzer (vario EL cube; Elementar, Germany) and the
results were listed in Table S1 and S2. The carbon content of WSOC were measured
using total organic carbon analysis (Vario TOC cube; Elementar) before acidifying
with phosphoric acid to remove inorganic carbon, while that of the MSOC fractions
were assessed using the method developed by Chen et al (Chen et al., 2017b). In short,
the extracted MSOC fraction was dried gently under nitrogen, and then re-dissolved
in 500 µL methanol. Subsequently, 50 µL of the solution was added to the clear quartz
filter (area: 1.5 cm²) until dry, and analyzed using the TOT standard method.

2.3 UV–Vis absorption spectra and EEM fluorescence spectra
The absorption and EEM spectra of the WSOC and MSOC samples were analyzed
using a UV-Vis spectrophotometer (UV-4802; Unico, China) and an Aqualog
fluorometer (Horiba Scientific, USA), respectively. The wavelengths used to
characterize the UV-Vis spectra were between 200 to 800 nm at a step size of 2 nm.
Purified water was used as a baseline correction before measure. Mass absorption
efficiency (MAE, m² g⁻¹ C) can be obtained as following equation (Li et al., 2018):

\[
MAE_\lambda = A_\lambda \cdot \ln(10) / (C \cdot L)
\] (1)
Here, $A_\lambda$ is the value of light absorption at given wavelength given by the spectrophotometer; $C$ (μg C mL$^{-1}$) is the concentration of WSOC and MSOC fractions; $L$ is the optical path length. Moreover, the pH of WSOC fraction was measured for all samples within the range of 5.5-6.5, generally thought it didn’t affect the absorbance according to prior study (Chen et al., 2016a).

The emission and excitation wavelengths of the fluorescence spectra were from 245 to 580 nm and 240 to 500 nm, respectively. The wavelength increments of the emission and excitation scans were 4.66 and 3 nm, respectively. Further, we subtracted the contributions of the solvents to the fluorescence spectra.

### 2.4 Ultrahigh resolution ESI FT-ICR MS analysis

Two fractions of six samples (IDs: 18 and 23 represented the mean fluorescence level of biomass burning; IDs: 38 and 46 represented anthracite and bituminous coal, respectively; IDs: 55 represents a day’s worth of samples of tunnel inlet and outlet, and IDs: 59 represents direct vehicle exhaust) were selected for FT-ICR MS analysis. To remove inorganic ions prior to instrumental analysis, the WSOC fraction was further adjusted to pH = 2 by the addition of hydrochloric acid (HCl), and then passed through a solid-phase extraction cartridge (Oasis HLB, 30 um, 60 mg/cartridge; Waters Corporation, USA). The constituent retained on the SPE cartridge were eluted with methanol containing 2% ammonia (v/v). Eluted samples were evaporated until dry under a gentle nitrogen gas stream. The extract by methanol was also evaporated under a gentle nitrogen gas stream for preparation.

We used the analysis method of FT-ICR MS described in detail in one of our previous studies (Mo et al., 2018). Briefly, ultrahigh resolution mass spectra were obtained using a solariX XR FT-ICR MS (Bruker Daltonics GmbH, Bremen, Germany) equipped with a 9.4-T superconducting magnet and an ESI ion source. The system was operated in negative ionization mode. The ion accumulation time was set to 0.6 s. The lower and upper mass limit was set to m/z 150 and 800 Da, respectively. The mass spectra were externally calibrated with arginine clusters using a linear calibration and then internally recalibrated with typical O$_2$S$_1$ class species peaks using...
quadratic calibration in DataAnalysis ver. 4.4 software (Bruker Daltonics). A typical mass-resolving power >450 000 at m/z 319 with <0.2 ppm absolute mass error was achieved. The mass spectra of field blank filters were analyzed to detect possible contamination following the same procedures. More data processing was presented in S1 of supplement.

2.5 PARAFAC analysis for EEM spectra

Parallel factor (PARAFAC) analysis with non-negativity constrains was used to explore the fluorescent components in dissolved BrC based on the method established by Murphy et al (Murphy et al., 2013; Andersson and Bro, 2000), which was performed using drEEM toolbox version 2.0 using a MATLAB software (http://models.life.ku.dk/drEEM). This method had been widely applied to the analysis of fluorescence spectra in aerosol (Chen et al., 2016b; Chen et al., 2016a; Matos et al., 2015; Wu et al., 2019). Absorbance measurements was used to correct the EEMs for inner filter effects (IFE) according to the previous studies (Luciani et al., 2009; Gu and Kenny, 2009; Fu et al., 2015). The highest light absorbance in the calibrated wavelength range in two fractions was not greater than 2 (mostly below 1 at 254 nm), which is appropriate for the inner filter corrections of the EEMs (Gu and Kenny, 2009; Murphy et al., 2013). Each EEM was normalized to the Raman peak area of purified water collected on the same day to correct fluorescence in Raman Units (RU) at excitation 350 nm, and corrected for the dilution factor (Murphy et al., 2013; Murphy et al., 2010). Additional, the signals of the first-order and second-order Rayleigh and Raman scattering in the EEM were removed by using an interpolation method (Bahram et al., 2006). Repeated convergence of the model was examined based on the iteration of the minimum squares principle. The exploration phases of 2- to 7-componet PARAFAC models were contained that evaluation of the shape of spectral loading, leverage analysis, examination of the core consistency, residual analysis, and split half analysis (Figure S2-S7). Finally, six component PARAFAC model was identified and successfully passed the split analysis.
with the split style of “S4C6T3” for WSOC and MSOC fraction in 60 samples, respectively.

3 Results and discussion

3.1 Emission Characteristics and Optical Properties of Extracts.

The PM, OC, and EC emission factors (EFs) of 27 biomass and 17 coal combustion experiments are summarized in Table S3. The relevant EFs of some of the biomass species were reported previously (Cui et al., 2018). In the current experiment, the EFs of PM, OC, and EC from burning 27 types of biomass were 15 ± 11 g kg⁻¹ fuel, 8.0 ± 6.4 g kg⁻¹ fuel, and 7.7 × 10⁻¹ ± 3.4 × 10⁻¹ g kg⁻¹ fuel, respectively. The EFs emitted from bituminous coal combustion (PM = 9.1 × 10⁻¹ ± 6.5 × 10⁻¹ g kg⁻¹ fuel, OC = 4.2 × 10⁻¹ ± 3.3 × 10⁻¹ g kg⁻¹ fuel, EC = 9.4 × 10⁻² ± 1.9 × 10⁻¹ g kg⁻¹ fuel) were much higher than those of anthracite combustion (PM = 1.5 × 10⁻¹ ± 8.9 × 10⁻² g kg⁻¹ fuel, OC = 1.2 × 10⁻² ± 4.5 × 10⁻³ g kg⁻¹ fuel, EC = 1.6 × 10⁻⁴ ± 1.4 × 10⁻⁴ g kg⁻¹ fuel) in the same stove. These differences can be attributed to the high volatile matter content of bituminous coal (Tian et al., 2017; Chen et al., 2005). Note that coal smoke was collected when the fire had been ignited using one third of the material, after which the remaining part was added. Thus, the results of our study were lower than the real values.

Mass absorption efficiency (MAE) can be used to characterize the efficiency of solar energy absorption, which is represented by the degree of conjugation and the amount of electron delocalization in molecules (Chen et al., 2016a). As shown in Figures 2b and S8b, and in Table S4, MAE at 365 nm (MAE₃₆₅) is significantly higher in the case of biomass burning and coal combustion than in vehicle emissions in the current study. Higher MAE₃₆₅ values were observed in the MSOC fractions collected from biomass burning (2.3 ± 1.1 m² g⁻¹C) and bituminous coal combustion (3.2 ± 1.1 m² g⁻¹C) compared to their WSOC fraction values. This may be due to the fact that these strongly light-absorbing fat-soluble components are likely to be large molecular weight PAHs, and quinones from biomass burning and fossil fuel combustion (Sun et al., 2007; Chen and Bond, 2009), while we obtained the opposite results in the case of
anthracite combustion and vehicle emissions. Moreover, the higher MAE$_{365}$ in biomass burning and bituminous coal combustion represented a stronger absorbing ability in the case of the MSOC fraction, which reflected greater variation in the chemical composition than in the WSOC fraction. The MAE$_{365}$ of biomass burning and coal combustion in the WSOC fraction was also higher than that of ambient aerosol and biomass and coal combustion experiments in a laboratory sampling system (Chen et al., 2018; Zhu et al., 2018; Yan et al., 2015; Li et al., 2018; Park and Yu, 2016) (Figure S4).

### 3.2 EEM spectra of dissolved BrC.

We applied the PARAFAC model (Murphy et al., 2013) to determine the underlying chromophore components of the 60 emission source samples. Six typically independent components of the WSOC fraction were resolved, as shown in the top of Figure 1 and Table 1. Compared with the previous studies, the EEM of P1 and P6 were similar to those for 7CM-C1 (the C1 component of a seven-component model) and 7CM-C3, pertaining to water-extracted matter in urban and forest area, and marine aerosols, in Japan (Chen et al., 2016b). Further, there were peaks in the emission wavelengths (> 400 nm) of P1 and P6, which were probably derived from conjugated systems (Chen et al., 2016b). The peak of the P3 component was almost located in region IV, which was categorized as a protein-like (cytidine) or tryptophan-like (peak T) fluorophore (Qin et al., 2018; Fan et al., 2016). Generally, peaks at shorter excitation wavelengths (< 250 nm) and shorter emission wavelengths (< 350 nm) are correlated with simple aromatic proteins such as tyrosine (Cory and Mcknight, 2005), which is quite similar to the peak of the P2 component observed in this study. According to a prior report, the spectra of the P5 component was also similar to tryptophan- and tyrosine-like components (Chen et al., 2017a). The spectra of the P4 component has been reported relatively rarely but is similar to previously observed peaks that are considered to arise mainly in surface water and algal secretions (Yu et al., 2015). Note that the origins and chemical structures of the
chromophores studied are not necessarily similar to those of chromophores with the same names in other types of organic matter.

**Table 1.** The maximum excitation and emission wavelengths of the PARAFAC components from the WSOC and MSOC fractions extracted from three origins

<table>
<thead>
<tr>
<th>PARAFAC component</th>
<th>Excitation maxima (nm)</th>
<th>Emission maxima (nm)</th>
<th>Assignment according to published papers</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>251, 314</td>
<td>415</td>
<td>HULIS-1, terrestrial humic-like component</td>
<td>(Chen et al., 2016b; Sgroi et al., 2017; Fu et al., 2015)</td>
</tr>
<tr>
<td>P2</td>
<td>254</td>
<td>337</td>
<td>Tyrosine-like</td>
<td>(Cory and Mcknight, 2005)</td>
</tr>
<tr>
<td>P3</td>
<td>287</td>
<td>360</td>
<td>Protein-like (cytidine) or tryptophan-like</td>
<td>(Qin et al., 2018; Fan et al., 2016)</td>
</tr>
<tr>
<td>P4</td>
<td>251</td>
<td>374</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P5</td>
<td>278</td>
<td>319</td>
<td>Protein-like fluorophores</td>
<td>(Fu et al., 2015)</td>
</tr>
<tr>
<td>P6</td>
<td>254, 371</td>
<td>485</td>
<td>terrestrial humic or fulvic acid-like component</td>
<td>(Chen et al., 2016b)</td>
</tr>
<tr>
<td>C1</td>
<td>308</td>
<td>356</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>&lt;250, 272</td>
<td>388</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>&lt;250</td>
<td>434</td>
<td>C2 for the urban ASOM samples</td>
<td>(Matos et al., 2015)</td>
</tr>
<tr>
<td>C4</td>
<td>257</td>
<td>360</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C5</td>
<td>284</td>
<td>328</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C6</td>
<td>269</td>
<td>310</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. The excitation-emission matrix (EEM) components spectra determined by parallel factor (PARAFAC) analysis of WSOC (top: P1-P6) and MSOC (bottom: C1-C6) extracted from three origins.

The results from the six-component model (abbreviated C1–6) of the MSOC fractions identified by PARAFAC, as described in the bottom of Table 1 and Figure 1, were obviously different to those obtained for the WSOC fraction. The peak of C1 component was similar to that of the P3 component of the WSOC fraction, but the excitation wavelength was higher, which indicated the presence of conjugated unsaturated bond systems shifting towards the high wavelengths of the C1 component (Matos et al., 2015). Moreover, as reported in a previous study, the C3 component was similar to the C2 component of urban alkaline-soluble organic matter (ASOM).
samples collected from the city of Aveiro, Portugal (Matos et al., 2015). Because the fluorescence spectrum of the MSOC fraction was poorly characterized, the molecular composition of the other fluorescent components was studied using FT-ICR MS.

The maximum fluorescence intensities ($F_{\text{max}}$) (Table S5, S6) is calculated by multiplying the maximum excitation loading and maximum emission loading for each component by its score (Murphy et al., 2013). Generally, changes in the relative abundance of a component ($F_{\text{max}}/\sum F_{\text{max}}$) could indicate changes in its overall importance, which had been successful applied to study the origins of chromophores (Yan and Kim, 2017; Chen et al., 2017a; Chen et al., 2016b; Wu et al., 2019). In the current study, the relative intensities of different fluorescent components in different types of samples was highly variable, depending on the sources. As shown in Figure 2a, P1 component was intense in the case of vehicle emission, accounting for an average of 30 ± 8.3% of the total fluorescence intensities of vehicle emission. P2 and P4 components were intense in the cases of biomass burning (mean: 33 ± 11% of fluorescence intensities of biomass burning) and coal combustion (mean: 34 ± 7.7%), respectively. The P3 components were almost equal across all samples. The possible reason is that the P3 components is similar to tryptophan-like compounds, where these are common to practically all published models and are likely to be found in almost all sources (Yu et al., 2015). It was obvious that P5 component was intense in direct vehicle exhaust (IDs: 59 and 60; mean: 30 ± 1.6%). In contrast, the fluorescence of P6 components was weak in any of the samples, but the P6 component in vehicle emissions (mean: 9.4 ± 2.2%) significantly exceeded those of biomass burning and coal combustion (both 2.5%). The above results clearly indicates that the chemical composition of chromophoric water-soluble BrC varies remarkably among sources.
Figure 2. (a) Relative abundance of each PARAFAC component, (b) mass absorption efficiency at 365 nm (MAE$_{365}$) values in WSOC fractions from three origins.

The relative intensities of the fluorescent components in the MSOC fraction exhibit similar characteristics to the WSOC fraction (Figure S8a). The C1 and C2 components was the substances with more intense in the case of biomass burning (mean: 38 ± 14 % and 21 ± 6.9%, respectively). C4 components was intense in samples of coal combustion (mean: 41 ± 6.0%). The levels of component C3 were not abundance between the three types of fuel tested. The C5 and C6 components was more intense in direct vehicular exhaust (IDs: 59 and 60; mean: 25 ± 6.8% and 50 ± 6.8%, respectively). Combining these results with the above-mentioned WSOC results and comparing the different characteristics and fuel source information, the fluorescent components obtained by EEM-PARAFAC can potentially assist with source apportionment for environmental monitoring applications.

3.3 Molecular composition of FT-ICR MS and chemical structures of chromophores

The relative abundances of the four compound groups (CHO, CHON, CHOS, and CHONS) in the WSOC fraction are presented in Figure S9. These results were consistent with previous results (Song et al., 2018), in which S-containing compounds were mainly found in coal combustion emissions. Conversely, our results
proved that N-containing substances were also abundant in coal combustion aerosols. One possible reason for this concerns the viable coal types; for example, significant differences were observed between water-extracts of IDs 36 (anthracite coal) and 46 (bituminous coal). More detailed information about the molecular compositions is provided in Tables S7 and S8, and Figure S10, S11 and S12.

The previous study reported that potential BrC chromophores were identified by determining those compounds in the region between Double bond equivalent (DBE) = 0.5 × C and DBE = 0.9 × C (in the coordinate axis, the x-axis is the C number and the y-axis is the DBE value) (Lin et al., 2018). To explore the possible chemical structures of dissolved chromophores, the methods of the O/C and H/C ratios of matter or functional groups were used to classify the ion groups of FT-ICR MS as listed in Figure 2. Furthermore, according to the all ions or potential BrC ions, there are total four classifications. The first method is to follow their O/C and H/C ratios of matter to classify all ions of FT-ICR MS; the second method is to follow their O/C and H/C ratios of matter to classify potential BrC ions; the third method is to follow their functional groups to classify all ions; the last method is to follow their functional groups to classify potential BrC ions. The relationship between the relative intensities of classified group of ions (the ratio of intensities of each ion group to total ion intensities) and the relative abundance of fluorescent components were presented in Table S9-S16. The results indicated that the method that sorted the potential BrC ion groups by their functional groups is best for explaining the relationship between the chemical composition and fluorescent components. For example, the presence of L-CHON groups with O/N ≤ 2 suggests that these reduced N compounds may be associated with alkyl amides and alkyl nitrile, as well as heterocyclic aromatic compounds with single N atoms (Alexander et al., 2009; Song et al., 2018). The H-CHON group with O ≥ 3, O/N > 2 and Almod > 0.5 suggests that these compounds contain O and N atoms, such as benzene rings substituted with O-containing groups (hydroxyl, and carboxyl) and nitro-aromatics (Chen et al., 2016b; Song et al., 2018; Lin et al., 2016). The H-CHOS group had O/S ≥ 4, suggesting the assignment of a sulfate group (-OSO3H). As sulfate groups carry four oxygen atoms and readily deprotonate
in ESI, they are more likely to be organosulfates (Jiang et al., 2016). The presence of the H-CHONS group suggested not only the assignment of a sulfate group (\(-\text{OSO}_3\text{H}\)), but also an additional one or two nitrooxy groups (\(-\text{ONO}_2\)) (Mo et al., 2018).
Table 2. The classification methods of ion groups of FT-ICR MS

<table>
<thead>
<tr>
<th>Function groups</th>
<th>Specific classification methods</th>
<th>H/C and O/C^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHO_1</td>
<td>O_1</td>
<td>Lipids</td>
</tr>
<tr>
<td>CHO_2</td>
<td>O_2</td>
<td>Lipids</td>
</tr>
<tr>
<td>L-CHON</td>
<td>O/N ≤ 2</td>
<td>H-Lignin</td>
</tr>
<tr>
<td>H-CHON</td>
<td>O/N &gt; 2</td>
<td>M-Lignin</td>
</tr>
<tr>
<td>L-CHOS</td>
<td>O/S &lt; 4</td>
<td>L-Lignin</td>
</tr>
<tr>
<td>H-CHOS</td>
<td>O/S ≥ 4</td>
<td>Carbohydrates</td>
</tr>
<tr>
<td>L-CHONS</td>
<td>O/S &lt; 7 (N_1); O/S &lt; 10 (N_2)</td>
<td>Tannins</td>
</tr>
<tr>
<td>H-CHONS</td>
<td>O/S ≥ 7 (N_1); O/S ≥ 10 (N_2)</td>
<td>Unsaturated hydrocarbons</td>
</tr>
</tbody>
</table>

Note that L, M, and H stands for low, moderate, and high, respectively; The lignin group is further divided into three subcategories on the base of their Al_{mod} and DBE (H-Lignin: 0.5 < Al_{mod} < 0.67; M-Lignin: 0 < Al_{mod} ≤ 0.5, DBE ≥ 4; L-Lignin: 0 < Al_{mod} ≤ 0.5, DBE < 4).

a: (Patriarca et al., 2018)
Figure 3. Pearson’s correlation coefficients (r) and significance levels (two-sided t-test) obtained from the correlation analysis between the relative intensity of the ion groups based on Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS), and the relative intensity of the (a) six components of the WSOC fractions and (b) six components of the MSOC fractions.

3.3.1 Composition of chromophores of WSOC

The relationship between the relative intensities of the classified ion groups of FT-ICR MS and the relative contents of the PARAFAC components in the WSOC fraction were presented in Figure 3a and Table S15. The P1 and P6 components were both negatively correlated with the H-CHOS group (p < 0.05). Considering that P1 and P6 components was intense in samples of vehicle emissions, the main compounds detected from this source were O,S$_1$–O$_{12}$S$_1$ class species with a wide range of C numbers (7–34) and double bonds equivalent (DBE) values (4–20), of which O$_4$S$_1$ and
O₃S₁ class species, which exhibit an R-OSO₃H structure, were the most abundant. Among these chemical formulas, we found that many aromatic organosulfate isomers with relatively high DBE values (≥ 4) were side chains or aromatic rings, and thus their chemical formulas could be those of alkylbenzene rings substituted with one sulfate and one hydroxyl group (Song et al., 2018), such as C₄H₁₀O₅S (DBE: 4) and C₁₀H₁₀O₅S (6). These structures were detected in humic-like substances (HULIS) from coal-smoke and SOA generated under all experimental conditions (Riva et al., 2015; Song et al., 2018) and were likely responsible for the P1 and P6 components.

The P4 component was positively correlated with the H-CHONS group (p < 0.05), suggesting nitrooxy-organosulfates (nitrooxy-OS) (Mo et al., 2018). Nitrooxy-OS is probably be formed by photooxidation of biogenic VOCs in smog chamber experiments conducted under high nitrogen oxide (NOₓ) concentrations (Lin et al., 2012). These results indicate that coal combustion is an important source of nitrooxy-OS, and this conclusion was consistent with the results of previous studies (Song et al., 2018). As shown in Figure 4, a wide range of C number (6–32) and DBE values (3–23) were observed in this group, and the DBE value increased with the C number. The main compounds in this group were O₃NₛS₁–O₁₃NₛS₁ class species, with O₃NₛS₁ class species being the most abundant. It is worth noting that most of the H-CHONS compounds had DBE values greater than or equal to 4, and the compounds with high intensities in the H-CHONS groups detected from coal combustion were C₆H₅O₇NS (5), C₁₀H₇O₅NS (8), and C₁₀H₆O₁₁NₛS (9). The most likely structure of these compounds is a benzene ring substituted with one sulfate and one or two nitrooxy groups (Song et al., 2018; Jiang et al., 2016). These were also detected in high concentrations in aerosols from Belgium and on a heavy PM₂.₅ haze day in Beijing city (Jiang et al., 2016; Kahnt et al., 2013).

The presence of the P5 component was highly correlated with the L-CHOS group (p < 0.05). This group was mainly composed of OₛS and OₛS₂ class species from direct vehicle exhaust emissions. Generally, these compounds contained too little oxygen to form sulfate functional groups, containing reduced sulfur (S), such as sulfonates, which was also detected in cloud water (Zhao et al., 2013). In these groups,
the main compounds of C_{26}H_{24}O_3S (15), C_{27}H_{26}O_3S (15), and C_{25}H_{22}O_3S (15) were homologues of C_{23}H_{20}O_3S (15), with the same general formula, C_{n}H_{2n-2}O_3S, and DBE values, of 15, likely corresponding to sulfonates of substituted benzopyrene (C_{20}H_{12}, DBE=15) (Blair et al., 2017). However, the P2 and P3 components were not significantly correlated with these ion groups.

### 3.3.2 Composition of chromophores of MSOC

Figure 3b and Table S16 show the relationship between the relative intensity of the classified ions groups and the relative contents of the PARAFAC components of the MSOC fraction. Only the C1 and C3 components were associated with one ion group (H-CHOS and CHO_{11}, respectively). Considering that the C1 component was highly intense in the case of biomass burning, the H-CHOS groups observed in samples of biomass burning were O_{2}S_{1}, O_{7}S_{1}, O_{10}S_{2}, O_{13}S_{1} class species, of which O_{10}S_{2} was the most abundant family. The probable structure of these species is an organosulfate with other O-containing functional groups, such as hydroxyl or carboxyl groups. This groups had a narrow range of C numbers (12–16) and DBE values (8), such as C_{13}H_{12}O_{10}S_{2} (8) and its homologues C_{13}H_{12}O_{10}S_{2} (8), C_{13}H_{16}O_{10}S_{2} (8), as well as C_{13}H_{16}O_{10}S_{2} (8), C_{16}H_{16}O_{10}S_{2} (8), C_{12}H_{16}O_{10}S_{2} (8), and C_{13}H_{12}O_{13}S (8).

C2 component was positively correlated with CHO_{11}, and negatively correlated with L-CHOS and L-CHONS groups. Figure 5 presented the DBE versus C number for the CHO_{11} group from samples of biomass burning, with the main compounds had C numbers of 17–20, DBE (10–11), and O numbers of 4–5. The potential structures of C_{18}H_{16}O_{4} (11) and C_{17}H_{16}O_{4} (10) are indicated as a and b, respectively, in Figure 5 and are suspected to be cyclic esters. The L-CHOS group were mainly O_{4}S_{2} class species, of which C_{12}H_{10}O_{4}S_{2} (8) was the main formula. The possible chemical structure is of two S-heterocycles connected to two ester bonds. Thus, C2 components may relate to ester compounds.

Further, the C5 component was positively correlated with L-CHOS and L-CHONS groups ($p < 0.05$), and the C6 component was positively associated with all S-containing groups ($p < 0.05$). We list some of the main formulas of these groups
detected in direct vehicle exhaust (IDs: 59), such as C_{12}H_{12}O_7S_2 (7) and C_{13}H_{14}O_7S_2 (7) for L-CHOS; C_{14}H_{16}O_7S_2 (8) and C_{15}H_{16}O_7S_2 (8) for H-CHOS; C_{36}H_{23}O_4NS (26) for L-CHONS; and C_{10}H_{6}O_11N_2S (9), C_{11}H_{6}O_11N_2S (9), C_{10}H_{10}O_13NS (8), C_{11}H_{10}O_13NS (8), C_{12}H_{14}O_12N_2S (10) for H-CHONS. The L-CHOS groups containing two S atoms is potential to be formed by sulfonation reactions, and their possible structure is of a fused benzene ring substituted with two sulfonates (-SO_3H). C_{36}H_{23}O_4NS may contain substantial quantities of S-containing compounds with reduced N (e.g., amide and nitrile, and heterocyclic aromatics) (Song et al., 2018). These results indicate that the C5 component is potentially related to sulfonates, but the structure of the C6 component is unclear. However, C4 components did not correlate with ion groups. Note that one class of compounds contributed to several fluorescent components, which indicated that numerous functional groups affect each component individually.

![Figure 4](https://doi.org/10.5194/acp-2019-584) Double bond equivalent (DBE) versus C number for the H-CHONS group of WSOC of coal combustion samples. The color bar and marker size denote the number of O atoms and the relative intensities of the compounds; a: C_{6}H_{5}O_7NS (DBE: 5); b: C_{10}H_{6}O_7NS (8); and c: C_{10}H_{6}O_11N_2S (9).
Figure 5. The DBE versus C number for the CHO>1 group of MSOC of biomass burning samples. The color bar and marker size denote the number of O atoms and the relative intensities of the compounds, a: C_{18}H_{16}O_{4} (11); b: C_{17}H_{16}O_{4} (10).

4 Conclusions

We conducted comprehensive measurements on light absorption, fluorescence, and molecular compositions of dissolved BrC derived from smoke particles during the simulated combustion of biomass and coal, as well as vehicle emissions. We observed the optical properties of the WSOC and MSOC fractions and observed that the light absorption of methanol-soluble BrC was stronger. Six fluorescent components were resolved in the WSOC and MSOC fractions by PARAFAC analysis, respectively. The relative intensities of the fluorescent components of the WSOC and MSOC fractions mainly depended on the different types of smoke particles, which were derived from several origins, suggesting that the fluorescent components varied from source to source. This result may be useful for fluorescence-based methods, which play an important role in the classification and source identification of BrC dissolved in the atmosphere.

We also discussed the possible structures of these chromophores. Our results indicate that these fluorescent components were mainly affected by functional groups, especially functional groups containing N and S. In the case of the WSOC fraction, P1 and P6 components were mainly associated with aromatic organosulfate compounds;
the P4 and P5 components were mainly associated with nitrooxy-OS compounds and sulfonates, respectively. However, we did not elucidate the structures of the P2 and P3 components. In the case of the MSOC fraction, the C1 component was mainly related to organsulfate compounds; the C3 component was related to CHO$_1$ groups; the C2 component was mainly correlated with esters; and the C5 component was related to sulfonates. The C6 component was correlated well with S-containing compounds. As with the P2 and P3 components, we know little about the structure of the C4 component. Our findings provide insights into the chemical structures of water- and methanol-soluble chromophores, and these results may be useful for further aerosol studies, for source apportionment of dissolved BrC based on EEM fluorescence.

Data availability. The data used in this study are available upon request; please contact Gan Zhang (Zhanggan@gig.ac.cn) and Jun Li (junli@gig.ac.cn)

Supplement. The supplement related to this article is available.

Author contributions. JT, GZ, JL, and YC designed the experiment. JT and MC carried out the measurements and analyzed the data. JT, TS, YH, and HJ organized and performed the samplings. JT (Jianhui Tang) and BJ supported the fluorescence and FT-ICR MS instrument. JT wrote the paper. JL, YM, JS, PP, and GZ reviewed and commented on the paper.

Competing interests. The authors declare that they have no conflict of interest.

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