

JGR Atmospheres

RESEARCH ARTICLE

10.1029/2019JD031149

Key Points:

- The total light absorption and fluorescence volume of particle extracts increased with the decrease in particle size
- The selected seven polycyclic aromatic hydrocarbons were positively correlated with the light absorption of particle extracts
- This study is the first to report the particle size distribution characteristics of chromophores in Linfen

Supporting Information:

Supporting Information S1

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Citation:

Chen, Q., Mu, Z., Song, W., Wang, Y., Yang, Z., Zhang, L., & Zhang, Y.-L. (2019). Size-resolved characterization of the chromophores in atmospheric particulate matter from a typical coal-burning city in China. *Journal of Geophysical Research: Atmospheres*, 124. https://doi.org/10.1029/2019JD031149

Received 11 JUN 2019 Accepted 30 JUL 2019

Size-Resolved Characterization of the Chromophores in Atmospheric Particulate Matter From a Typical Coal-Burning City in China

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Abstract This study reports the size-resolved characterization of the chromophores in atmospheric particulate matter in Linfen, a typical coal-burning city in China. The optical properties of both the water-soluble and water-insoluble chromophores in atmospheric particulates are studied using excitation-emission matrix spectroscopy and follow the parallel factor analysis of excitation-emission matrix data. The mass absorption efficiency and normalized fluorescence volume by mass concentration of the organic carbon in methanol-soluble matter in the particulate samples are stronger than that of the water-soluble matter. We found that the total absorption (Abs), fluorescence volume (FV), mass absorption efficiency, and normalized fluorescence volume of particle extracts with sizes less than 10 μ m increased with the decreasing particle size. The total concentration of the selected seven polycyclic aromatic hydrocarbons was positively correlated with the Abs₃₆₅ and FV of both the water-soluble matter and methanol-soluble matter, but the average contribution of the selected polycyclic aromatic hydrocarbons to the total Abs and FV was very small (<3%). This study is the first to report a size-resolved characterization of the chromophores in atmospheric particulate matter. Humic-like substances tend to be present in small particles, and tryptophan-like and tyrosine-like components tend to increase with increasing particle size.

1. Introduction

Brown carbon (BrC), an organic component of aerosols with the capacity to absorb visible light, has been regarded as a potential contribution to the nonnegligible positive radiative forcing exacerbating the Earth's greenhouse effect (Alexander et al., 2008; Feng et al., 2013). Recently, it has been shown that the environmental effects of chromophores include not only photolysis but also the formation of triplet substances (De Laurentiis et al., 2013; Smith et al., 2014; Richards-Henderson et al., 2015). Therefore, it is essential to characterize the physicochemical characteristics of these chromophores to understand their sources and formation mechanisms and to quantitatively assess their effects on radiative forcing in the Earth's atmosphere and on the heterogeneous chemical reactions among atmospheric particulates.

BrC can be derived from both primary sources and secondary processes. Zhang, Lin, et al. (2013) found that water-insoluble BrC was positively correlated with elemental carbon (EC) in the Los Angeles Basin, indicating that BrC was mainly derived from a primary combustion source. Biomass combustion (BBOA) is one of the most important primary sources of atmospheric BrC (Moschos et al., 2018), even on the Tibetan Plateau (Wu et al., 2018). Coal combustion can also produce abundant BrC (Bond et al., 2002; Sun et al., 2017; Wang et al., 2016; Zhang et al., 2018). At present, coal combustion is still the main method of producing electricity in China and is also the main method of central heating in northern China (Liu et al., 2009; Liu et al., 2016; Zhang & Smith, 2007; Zhi et al., 2008). Therefore, coal combustion may also be an important source of BrC in cities or regions where coal use is concentrated, such as Shanxi Province, including Linfen city. Linfen is the one of largest coal-producing, coke-producing, and coal-burning areas in China. It could be regarded as a "coal-burning city." The secondary formation process of BrC includes several known reactions, such as benzene ring-containing volatile organic compounds, which can form nitrophenolic BrC compounds by atmospheric chemical oxidation in the presence of NOx (Lin, Liu, et al., 2015). The reaction of ammonia and ketone/aldehyde can produce N-containing chromophores (Lin, Liu, et al., 2015; Powelson et al., 2014).



However, atmospheric oxidation processes, including photochemical oxidation, tend to decompose/bleach chromophores (Wong et al., 2017; Zhao et al., 2015). Several previous studies have found that the concentration of atmospheric BrC in winter is significantly higher than that in summer. This phenomenon is explained by the fact that chromophores are photobleached under relatively stronger light conditions in summer than in winter (Chen, Ikemori, & Mochida, 2016).

BrC may contain multiple compounds in actual aerosol samples. After extracting BBOA with acetonitrile as an extraction solvent, Lin et al. (2016) found that approximately half of the absorption of the solvent-extractable fraction of BBOA was attributed to 20 strong chromophores, including nitrophenolic compounds. However, the quantitative analysis of nitro-aromatic compounds accounts for only a small fraction of the overall absorption by water-soluble BrC in ambient particulates (Zhang, Lin, et al., 2013). Budisulistiorini et al. (2017) analyzed BBOA samples using liquid chromatography-mass spectrometry. They identified 41 light-absorbing compounds, including oxygenated-conjugated compounds, nitro-aromatics, and S-containing compounds, which account for 24% of BBOA but only 0.4% of the actual atmospheric particulate matter (PM). Thirty major BrC compounds are identified as N-containing compounds in the solution produced through reactions of methylglyoxal and ammonium sulfate (Lin, Laskin, et al., 2015). Chen, Ikemori, and Mochida (2016) also reported that chromophores may be low-polarity compounds containing heteroatoms, such as N and O, and they also indicated that water-insoluble chromophores contributed significantly to the light absorption and fluorescence properties of atmospheric PM (Chen, Ikemori, & Mochida, 2016and Chen et al., 2017). Polycyclic aromatic hydrocarbons (PAHs) may be important components of water-insoluble BrC. It has been found that PAHs and their oxygenated derivatives (O-PAHs) are positively related to the light absorption properties of both water-soluble and methanol-soluble components of atmospheric particulates (Huang et al., 2018), whereas the detected PAHs and O-PAHs contributed only a small fraction of the light absorption in the extraction components (Chen, Ikemori, & Mochida, 2016; Huang et al., 2018).

The composition of BrC in actual atmospheric particulates is very complex, similar to the conclusions regarding complex organic aerosols by Andreae (2009). Although we try to identify each of the chromophore molecules and structures, these efforts may not be necessary, and this work is also unlikely to be completed. We can classify the complex chromophores into several categories according to their physicochemical properties so that the classification of categories can distinguish different sources or represent similar environmental behaviors. The three-dimensional excitation-emission matrix (EEM) method can separate chromophores into several categories according to excitation-emission wavelengths for chromophores that may not be distinguishable by UV-visible absorption spectroscopy (Chen, Miyazaki, et al., 2016and Chen, Ikemori, & Mochida, 2016). Although the EEM method has more difficulty identifying individual molecules than liquid chromatography-mass spectrometry, the EEM method can easily classify compounds with similar optical characteristics, each of which may represent similar chemical structures and photochemical features, and the types and relative contents of chromophores may be used to trace the sources of the chromophores (Chen, Miyazaki, et al., 2016; Yan & Kim, 2017).

Previous studies have characterized the light absorption properties of atmospheric particulate BrC with different particle sizes, and they have revealed that the light absorption capacities are different for particles with different sizes, reflecting differences in the types and sources of the chromophores (Liu et al., 2013; Lorenzo et al., 2018). However, few studies have used the EEM method to study the optical characteristics of chromophores in atmospheric particles with different particle sizes (Aryal et al., 2015). On the other hand, the solvent extraction method can extract chromophores with different polarities from atmospheric particulate samples according to the polarity of the solvent. Most BrC can reportedly be extracted with methanol (Cheng et al., 2016). Therefore, water-soluble and water-insoluble chromophores can be extracted by a continuous extraction method with water followed by methanol (Chen, Ikemori, Higo, et al., 2016and Chen, Ikemori, & Mochida, 2016). Simultaneous study of the optical properties of water-soluble and water-insoluble areosol components contributes to a comprehensive understanding of the types of chromophores and optical properties of atmospheric PM, as well as the processes of oxidation and transformation of chromophores.

In this study, the size-resolved characterization of the water-soluble and water-insoluble chromophores in atmospheric PM at Linfen, a typical coal-burning city, was studied by EEM analysis and the parallel factor (PARAFAC) data analysis method. The differences in optical properties (light absorption and



fluorescence) between winter and summer samples were compared, and the contribution of PAHs to the optical properties of particulate samples was quantitatively evaluated based on the quantitative analysis of PAHs in the samples. This study also explored the relationship between light absorption and fluorescence properties and the relationships between optical properties and PAHs, organic carbon (OC), and EC. The possible source of chromophores is preliminarily discussed on the basis of the chromophore type analysis. The results of this study help to deepen the understanding of the physicochemical properties and sources of chromophores, especially the particle size distribution characteristics of different types of chromophores.

2. Experimental Section

2.1. Sample Collection

The sampling site was at Hongdong ($36^{\circ}23'N$, $111^{\circ}40'E$), a county town of Linfen city, which is located in Shanxi, China. The surrounding sampling environment is mainly a rural environment. There are no factories in the vicinity. The sampling altitude was 464 m. The sampler was approximately 10 m from the ground. Aerosol samples were collected with a Thermo-Anderson Mark II sampler, which can segregate particle samples into nine size levels and has a working flow rate of 28.3 L/min. Particulates with different particle sizes were collected on quartz fiber filters. The particle sizes of S0–S8 are 9.0–10.0, 5.8–9.0, 4.7–5.8, 3.3–4.7, 2.1–3.3, 1.1–2.1, 0.65–1.1, 0.43–0.65, and <0.43 μ m, respectively. PM with particle sizes of S2–S8 was collected on a full-sized filter with a diameter of 81 mm; particles with particle sizes of S0–S1 were collected on a ring filter with an outer diameter of 81 mm and an inner diameter of 22 mm. The sampling duration was from 26 January to 4 February 2017, and each sampling event lasted for 23.5 hr from 8:00 in the morning to 7:30 in the next morning. Before collection, all the filters were baked at 450 °C for 4.5 hr; the sampling environment is shown in Tables S1 and S2 in the supporting information.

2.2. Sample Extraction

Continuous solvent extraction was employed to extract water-soluble matter (WSM) and methanol-soluble matter (MSM) from aerosols. Briefly, WSM samples (0.16 cm² for sizes of $<0.43 \mu m$ and approximately 0.7 cm^2 for other particle size samples) were ultrasonically extracted for 15 min with 3-mL ultrapure water. After the extraction, MSM was extracted using 3-mL MeOH (Fisher Chemical Company, Shanghai, China) from the same samples and in the same manner as the water extraction. Different filter areas were used in the extraction process to reduce the concentration differences in the extracted PM of different sizes. Both WSM and MSM extracts were filtered through 0.22-µm polytetrafluoroethylene filters (Jinteng, Beijing, China). To determine the extraction efficiency of water-insoluble OC and BrC using the procedure, after extraction with water and MeOH, the particulate residues were also consecutively extracted with dichloromethane (DCM). The results show that only 14% of the BrC was extracted by DCM after extraction with water and MeOH (Figures S1 and S2 and Table S3). These results demonstrate that the extraction procedure can extract a majority of the extractable BrC in atmospheric aerosols. Two groups of samples were extracted twice by water to obtain the first water extraction and the second water extraction. The EEM and absorption characteristics of different extractions were determined to obtain the extraction efficiency of water-soluble BrC. We also extracted two groups of samples from the water at the same time. MeOH was used to extract the samples three times, and then they were extracted with DCM to obtain the first, second, and third MeOH extractions and DCM extraction, respectively. We determine the EEM and absorption characteristics of different extractions to quantify the extraction efficiency of water-insoluble BrC. The results show that the extraction efficiency of BrC is 80% for water and MeOH extraction (Figures S1-S3 and Tables S3 and S4). After determining the optical properties, the OC content in different extractions was quantified via an OC/EC analyzer to obtain the OC extraction efficiency. Detailed results are given in the following section.

2.3. Instrumental Analyses

2.3.1. OC/EC Analyses

Briefly, OC and EC were analyzed using a semicontinuous OC/EC analyzer (Model 4, Sunset Lab. Inc.; Oregon, USA). A 2.27-cm² subsample punched from each quartz filter was analyzed in accordance with the NOISH 5040 protocol (Lin et al., 2009; Tables S6 and S7).

2.3.2. TOC Analyses

The water-soluble organic carbon (WSOC) concentration was analyzed by an automated TOC- L_{CPH} analyzer (Shimadzu, Japan) after 15 min of extraction of subsamples with ultrasonication. All WSOC concentrations



were blank corrected. The concentration of OC in MSM was calculated as the difference between the OC and WSOC concentrations. The calculation assumed that all water-insoluble organic carbon (WISOC) in the aerosols can be extracted with MeOH (Cheng et al., 2016; Liu et al., 2013; Mihara & Michihiro, 2011). Additional experiments have shown that only a small amount of OC (6%) were extracted with DCM after MeOH extraction (Table S5). These results demonstrated that MeOH can extract the majority of the extractable OC in atmospheric aerosols.

2.3.3. PAH Analyses

The target PAHs were analyzed using an optical-4 thermal-desorption injection port coupled with GC7890B/ MS5977A (Agilent Technologies; Clara, CA), and the analysis protocol has been described in the previous studies (Han et al., 2018).

2.3.4. Spectrophotometer Analysis

The extracts of WSM and MSM in a quartz cell $(1 \text{ cm} \times 1 \text{ cm})$ were analyzed by an AquaLog fluorescence spectrometer (HORIBA, USA). Both UV-Vis absorption spectra and EEM spectra can be obtained simultaneously by the fluorescence spectrometer. The UV-Vis absorption spectra of extracts were recorded in the wavelength range of 200 to 600 nm. The EEM was recorded in the wavelength range of 210 to 600 nm for excitation and 250 to 800 nm for emission with a 5-nm interval. Before sample analysis, the pure solvents of water and MeOH were analyzed using a fluorescence spectrometer to create the reference signal.

2.4. Data Analysis

2.4.1. UV-Vis Absorption Spectra

The UV-Vis absorption spectra of extracts were recorded in terms of absorbance. The UV-Vis absorption spectra of extracts were baseline corrected by subtracting the spectra of the absorbance at 600 nm for each sample. This correction can lead to a small underestimation of the absorbance because the extracts have weak light absorption at 600 nm. Based on the data sets reported by previous studies (Chen, Miyazaki, et al., 2016, and Chen et al., 2017), the underestimation associated with this correction is estimated to be approximately <20% at 500 nm, <5% at 400 nm, and <1% at 300 nm. Based on the light absorption spectra, the MAEs (m²/g[OC]) of the OC in the extracts were calculated using $MAE_{\lambda} = \ln(10) Abs_{\lambda}/C_{oc}$ (where $Abs(\lambda)$ is the light absorption coefficient [m⁻¹] and C_{oc} is the concentration of organic carbon in the extract [g[OC]/m³]). The Ångström exponent (Å) for each extract was fitted in the wavelength range of 280–550 nm using $MAE_{\lambda} = a \lambda^{\hat{A}}$. The total light absorption values of the extracts were calculated from the MAE of the OC and the atmospheric concentrations using $Abs_{\lambda,OC total} = MAE_{\lambda,WSM} \cdot C_{WSOC} + MAE_{\lambda,MSM} \cdot C_{WISOC}$. The light absorption values of EC in the studied samples were calculated using $Abs_{\lambda,EC} = MAE_{\lambda,EC} C_{EC}$ (where C_{EC} is the concentration of EC in the atmosphere [μ g/m³] and the MAE of EC at 550 nm and the Å are assumed to be 7.5 m²/g and 1, respectively; Bond & Bergstrom, 2006; Chen, Miyazaki, et al., 2016, and Chen, Ikemori, & Mochida, 2016).

2.4.2. EEM and PARAFAC analysis

The postprocessing of the EEMs follows the procedures described elsewhere (Chen, Miyazaki, et al., 2016; Murphy et al., 2010). Briefly, the raw EEMs were first calibrated with the spectral correction factors of the spectrometer, which reflects the deviation of the instrument itself, including the light soursce. The second correction is an inner filter correction, which is based on the corresponding UV-Vis absorbance spectra of the extracts. The light absorbance of the extracts in the calibrated wavelength range was lower than 0.7, which is appropriate for the inner filter corrections of the EEMs (Gu & Kenny, 2009). After the inner filter correction, the signal intensity of the EEMs was normalized to the Raman unit (RU) of water (Lawaetz & Stedmon, 2009). The fluorescence volume (FV, RU-nm²/m³) of extracts in the atmosphere was calculated based on the EEMs in the excitation wavelength of 210–450 nm and in the emission wavelength of 250–600 nm. The FV was normalized, that is, NFV (RU-nm²-[mg/L]⁻¹), using NFV = FV/ C_{oc} (where C_{oc} is the concentration of OC in the atmosphere [mg/m³]).

Different types of chromophores in the aerosol samples were mathematically resolved and identified through the PARAFAC analysis of the EEMs (n = 396) using the drEEM toolbox version 0.2.0 for MATLAB (Murphy et al., 2013; http://www.models.life.ku.dk/deEEM). A six-component PARAFAC solution was adopted by comparisons of the residual errors and by visual inspection for the two- to nine-component PARAFAC model (Figure S4). One of the PARAFAC components was excluded because it was a component from an instrument artifact (Chen, Ikemori, & Mochida, 2016). Ultimately, five EEM components were determined and assigned to different types of chromophores (Figure S5).



Journal of Geophysical Research: Atmospheres



Figure 1. Temporal variations in the concentrations of $PM_{10}(a, b)$, OC (a, b), EC (a, b), WSOC (c, d), and WISOC (c, d) and light absorption by aerosol extracts at 365nm (Abs₃₆₅; e, f) and FV (e, f) in the EEMs for WSM and MSM in winter (a, c, and e) and summer (b, d, and f). PM = particulate matter; OC = organic carbon; WSOC = water-soluble organic carbon; EC = elemental carbon; WSM = water-soluble matter; FV = fluorescence volume.

2.4.3. Contributions of PAHs to the Optical Properties of Aerosol Extracts

The target PAHs were analyzed using an optical-4 thermal-desorption injection port coupled with GC7890B/ MS5977A (Agilent Technologies; Clara, CA), and the protocol was analyzed as described in previous studies (Han et al., 2018). Seven standard PAHs, including acenaphthylene, phenanthrene, anthracene, fluoranthene, benzo[a]anthracene, benzopyrene, and benzo[ghi]perylene MeOH (1 mg/L), were analyzed by an AquaLog fluorescence spectrometer. Both the UV-Vis absorption spectra and EEM of these PAHs were obtained to evaluate the contributions of PAHs to the optical properties of the aerosol extracts based on quantitative analysis of the PAHs in the studied samples (Song et al., prepared paper).

3. Results and Discussion

3.1. Concentrations of PM, OC, EC, WSOC, and WISOC

Figures 1a–1d show the seasonal variations in the mass concentrations of PM, OC, EC, WSOC, WISOC, and PAHs in PM₁₀ (extraction information is shown in the Tables S6 and S7). The mass concentrations of PM₁₀ in winter and summer ranged from 471 to 670 μ g/m³ and 224 to 333 μ g/m³, respectively. The average mass concentration of PM₁₀ in winter was approximately 2 times higher than in summer. The average concentrations of OC, EC, WSOC, and WISOC were 98.13 ± 19.63, 7.53 ± 2.78, 30.79 ± 8.74, and 67.35 ± 16.84 μ g/m³ in winter and 28.81 ± 9.02, 3.81 ± 1.51, 12.59 ± 3.18, and 16.25 ± 6.08 μ g/m³ in summer. The relatively high concentrations of PM₁₀, OC, EC, WSOC, and WISOC in winter are likely related to winter heating in Linfen and the sharp increase in coal or the burning of other fuels in the cold season (Liu et al., 2015; Wang et al., 2017).

Figures 2a–2e show the distribution of the mass concentrations of PM, OC, EC, WSOC, and WISOC with particles of different sizes. PM with particle sizes of <0.43 and 1.1–2.1 μ m exhibits peak values; however, the peaks in the summer samples are not obvious. Except for WSOC in winter, the OC, EC, WSOC, and WISOC are higher for particle sizes of <0.43 μ m than other particle sizes. Both winter and summer samples indicate that fine particles tend to be abundant in carbonaceous particle (Fang et al., 2017; Herckes et al., 2006; Hu et al., 2012). The relative contributions of PM, OC, EC, WSOC, and WISOC masses are also shown





Figure 2. Particle size and seasonal distributions of the concentrations of $PM_{10}(a)$, OC (b), EC (c), WSOC (d), WISOC (e), and PAHs (f), and the light absorption at 365 nm (Abs₃₆₅; g, h, and i) and FV (j, k, and l) in the excitation-emission matrices for WSM (g, j), MSM (h, k), and both water-soluble and MSM (i, l). PM = particulate matter; OC = organic carbon; EC = elemental carbon; WSOC = water-soluble organic carbon; WISOC = water-insoluble organic carbon; WSM = water-soluble matter; PAH = polycyclic aromatic hydrocarbon; MSM = methanol-soluble matter; FV = fluorescence volume.

in Figure 3. The results show that EC and WISOC are mainly distributed over sizes of $<0.43\mu$ m, accounting for 60% and 35% in winter, respectively, obviously higher than the 26% and 19% in summer, respectively. Therefore, the contribution of combustion sources to fine particles in winter is greater than that in summer, which is related to the sources. The difference in the particle size distribution of EC between winter and summer may be related to the seasonal variations in the major emission sources for EC and WISOC (Huang et al., 2018; Yang et al., 2018; Zhang, Zotter, et al., 2013). In addition, this study found that the concentration distribution of PM, OC, and WSOC among particles of different sizes did not differ greatly between winter and summer. The seasonal variation and size distribution characteristics of the mass concentrations of PAHs in PM₁₀ are described in detail elsewhere (Song et al., submitted paper).

3.2. Optical Properties of Aerosol Extracts

The aerosol optical properties differ between winter and summer. As Figures 1e and 1f show, the average total absorbance Abs_{365} and FV are $184 \pm 46 \text{ Mm}^{-1}$ and $(1.1 \pm 0.2) \times 10^5 \text{ RU-nm}^2/\text{m}^3$, respectively, in winter and $32 \pm 11 \text{ Mm}^{-1}$ and $(1.6 \pm 0.5) \times 10^4 \text{ RU-nm}^2/\text{m}^3$, respectively, in summer. The Abs_{365} and FV values in winter are 5.8 and 6.9 times higher than those in summer, indicating that chromophores were more abundant in winter. The average Abs_{365} of WSM in winter was $33 \pm 7 \text{ Mm}^{-1}$, which is higher than the reported values of water-soluble BrC ($24 \pm 19 \text{ Mm}^{-1}$) in winter in Kanpur, India, in 2016 (Satish et al., 2017) and water-soluble BrC ($10 \pm 7 \text{ Mm}^{-1}$) in winter in Beijing, China, in 2011 (Cheng et al., 2016). The mass absorption capacity of MAE₃₆₅ and the fluorescence ability of NFV were also different in different seasons, and the variation patterns were similar to those of the total light absorption and total fluorescence ability. In winter, the average values of MAE₃₆₅ and NFV were $1. \pm 0.2 \text{ m}^2/\text{g}$ and $1,148 \pm 103 \text{ RU-nm}-[\text{mg/L}]^{-1}$, respectively.



Journal of Geophysical Research: Atmospheres

10.1029/2019JD031149



Figure 3. Relative contributions of PM_{10} , EC, OC, WSOC, and WISOC masses, and the light absorption (Abs₃₆₅) and FV for WSM and MSM as a function of particle size in winter and summer. PM = particulate matter; OC = organic carbon; EC = elemental carbon; WSOC = water-soluble organic carbon; WISOC = water-insoluble organic carbon; WSM = water-soluble matter; MSM = methanol-soluble matter.

Compared with winter, the MAE and NFV in summer were lower, $1.1 \pm 0.3 \text{ m}^2/\text{g}$ and $573 \pm 105 \text{ RU-nm-}[\text{mg/L}]^{-1}$, respectively. The results indicate that more light absorption and fluorescence components were found in the organic components of PM in winter, which was likely due to the photolysis of chromophores in summer (Chen, Miyazaki, et al., 2016; Gao & Zhang, 2018; Lukacs et al., 2007). The variation trends of FV and absorbance of atmospheric PM are consistent among different samples. Our results show that the fluorescence intensity depends on the absorbance (see panels a and b in Figures S6 and S7). Thus, the sample absorbance and fluorescence may be generated from the group of chromophores, and a more detailed discussion is given in section 3.4.

The optical properties of particles with different particle sizes are different. As shown in Figures 2g–2l, the smaller particles have higher absorbance and fluorescence values. There are two peaks in Abs_{365} at particles sizes of <0.43 and 0.65–1.1 µm in winter, while the FV increases gradually with decreasing particle size, with no obvious second peak value. We found that both the Abs_{365} and FV of MSM are higher than those of WSM, that is, approximately 5 times higher in winter and approximately 3 times higher in summer. Hence, water-insoluble chromophores are more abundant than water-soluble chromophores, and this result is similar to that reported by Chen, Ikemori, and Mochida (2016). We found that the correlation between fluorescence and absorbance for particle sizes of <0.43 µm is significantly different from that in other particle size ranges, indicating a difference in the BrC and chromophore species in particles with diameters of <0.43 µm (as panels a and b in Figure S6). This conclusion is verified by the PARAFAC analysis of the EEMs, and detailed results are given in section 3.5. The morphology of the particles affects the optical properties in the actual atmosphere (Li et al., 2013). This assessment did not examine the effect of particle size and shape on light absorption and fluorescence properties (Chen et al., 2017; Chen, Ikemori, & Mochida, 2016).

The mass absorbing ability MAE_{365} and fluorescence ability NFV of OC vary with the size of the particles and are similar to the patterns of the total Abs and FV with respect to the particle size distribution. Figure 4 shows that both the WSM and MSM of finer particles have larger MAE and NFV values than that of large particles. Figure 4e shows that the average MAE and NFV values of OC in ultrafine particles (<0.43 μ m) are



Aerodynamic diameter (µm)

Figure 4. Particle size and seasonal distributions of mass absorption efficiency at 365 nm (MAE₃₆₅) and the NFV for WSM (a, c, and e) and MSM (b, d, and f). (e and f) The average value of MAE and NFV in summer and winter respectively for WSM and MSM extracts. WSM = water-soluble matter; MSM = methanol-soluble matter; MAE = mass absorption efficiency; NFV = normalized fluorescence volume.

approximately 2–3 times higher than those of the larger particles with diameters of 1.1–10 μ m. For WSM (Figure 4a), the MAE of OC in 0.43- to 2.1- μ m particles in summer and winter is similar, whereas the MAE of OC for other size particles is approximately 2 times higher in summer samples than in winter samples. This pattern may be related to secondary chromophore generation in summer, and the generated chromophores may be mainly present for sizes of <0.43 and >2.1 μ m. In contrast, the MSM does not obviously exhibit this phenomenon, indicating that the secondary generation of chromophores in summer may be mainly limited to WSM. In terms of the fluorescence ability of WSM (Figure 4c), the summer samples are always larger than winter samples at different particle sizes. However, for the MSM with a large particle size (>2.1 μ m in Figure 4d), the fluorescence ability is higher in winter than in summer (by approximately 2 times). This pattern may be due to the relatively large amount of N-containing compounds in the large particles in winter, and this hypothesis is supported by the abundance of amino acid-like chromophores, as detailed in section 3.5.

The results in Figure 5c and 5d show that the relative contributions to the absorbance at different wavelengths by different particle sizes varies slightly, and no component varies abruptly with the variation in wavelength. Moreover, the average absorbance of BrC decreases gradually with increasing wavelength (Figures 5a and 5b and S8a–S8d). The variation trend of the absorbance of BrC with wavelength can be described by the parameter AAE (wavelength dependence index): MAE (λ) = a· λ^{-AAE} , where λ is the wavelength (280–600 nm) and a is related to the light absorption properties of the substance. The magnitude of the AAE can reflect the difference in BrC source and atmospheric chemical processes (Lack et al., 2013). As shown in Figure 6, the AAEs of WSM and MSM ranged from 3.5–6.7 to 5.5–7.2, respectively, which is





Figure 5. Particle size-resolved UV-visible absorbance spectra (a and b) and relative contributions of light absorption by the aerosol extracts (c and d) in summer (a and c) and winter (b and d).

similar to reported values in Nagoya (Chen, Ikemori, & Mochida, 2016). The AAE value of WSM in winter (4.2 ± 0.5) was significantly lower than that of WSM in summer (6.1 ± 0.2) and MSM in winter (6.7 ± 0.5) and summer (6.0 ± 0.3) , which indicates a significant difference in the chemical composition of BrC. The AAE value has been correlated with the polarity of BrC. Chen, Ikemori, and Mochida (2016) found that the greater the polarity, the larger the AAE value. The AAE increase indicates that more polar BrC is formed in summer. This study uses the ratio of MAE at 250 nm to that at 365 nm (E_2/E_3) to identify possible aromatic compounds in the aerosols (Chen, Ikemori, & Mochida, 2016; Duarte et al., 2005). As shown in Figures 6c and 6d, the E_2/E_3 value of WSM in winter is 4.2 ± 0.8 , significantly less than that of WSM in summer (8.2 ± 1.6) and MSM in winter and summer (5.7 ± 0.8), which indicates that the WSM in winter may contain more aromatic and/or higher molecular weight compounds (Duarte et al., 2005; Chen, Ikemori, & Mochida, 2016

The AAE and E_2/E_3 of BrC in particles of different sizes are also different. The AAE and E_2/E_3 of WSM in summer show a trend of increasing with increasing particle size. In contrast, the WSM samples in winter show a trend of first increasing and then decreasing. This pattern indicates that the aromatic abundance/ molecular weight of the BrC compounds in small-particle WSM is higher than that in large-particle WSM in summer, while the aromatic abundance/molecular weight of the BrC compounds in large-particle WSM is higher than that in small-particle WSM in winter. For MSM samples, the AAE and E_2/E_3 do not change significantly with particle size. However, the AAE and E_2/E_3 of MSM are higher in winter than in summer, indicating that water-insoluble BrC in summer has more aromatic properties than that in winter.

3.3. Contributions of PAHs to the Optical Properties of Aerosol Extracts

The above results show a significant contribution of water-insoluble components to the total optical properties of atmospheric PM. In this study (Figures 1e and 1f), atmosphere PM accounted for an average of 82% and 85% of the total light absorption and fluorescence intensity, respectively. PAHs may be important light-absorbing and fluorescent substances in the water-insoluble components. Therefore, this study quantitatively evaluated the contribution of seven PAHs to the light absorption and fluorescence properties of MSM, and the results are illustrated in Figures 7–9. As shown in Figure 7, the Abs₃₆₅ values of the selected PAHs are approximately 3 times higher in winter than in summer, but the maximum contribution does not exceed 7% of the total light absorption by MSM in the 280- to 550-nm wavelength range. The maximum Abs contribution is at 430 nm, mainly due to benzopyrene (Figure S9). The absorbance spectra of the selected PAHs show significant specific material absorption characteristics: A few typical strong absorption peaks are present, whereas the absorbance spectra of the MSM extraction components are smooth; thus, significant differences in the shapes of the absorbance spectra exist between the PAHs and the MSM extracts. The results indicate that the BrC composition of MSM is complex, and other substances in MSM have a greater impact than the selected PAHs. This result is similar to the results of previous studies. For example, Chen et al. (2016) reported that the contributions of the PAHs to light absorption are only 19%–31% of the total absorption of the water-insoluble organic matter in the total suspended particles in Nagoya. Moreover, Huang et al. (2018) indicated that their measured eighteen PAHs and their carbonyl oxygenated polycyclic aromatic hydrocarbons (carbonyl-OPAHs) accounted for only ~1.7% of the total absorption of methanol-soluble BrC in PM_{2.5} in Xi'an.

The contribution of the selected PAHs to the MSM fluorescence intensity is also limited. Figure 8 shows that the fluorescence intensity of the selected PAHs is approximately 10 times higher in winter than in summer, but the maximum contribution is less than 10% of the fluorescence intensity by MSM, and the maximum fluorescence contribution is roughly at an excitation of 210 nm and an emission of 450 nm. This result indicates that in addition to the selected PAHs, other compounds also play a major role in fluorescence. In addition, the EEM spectra of the seven selected PAHs showed different fluorescence peaks with wavelength position and fluorescence (Figure S10). Thus, even the same type of substance shows obvious differences in fluorescence properties due to small differences in chemical structure, indicating that the fluorescence means are very sensitive to specific chemical structures. Figures 8a and 8b show that the EEM spectra of MSM in winter and summer are significantly different. The signals are mainly concentrated at an excitation of 230 nm and an emission of 370 nm in winter. However, in summer, there are strong signals in the smaller excitation and emission bands, indicating that there are significant differences in the type and relative proportions of chromophores in winter and summer.

The selected PAHs have different contributions to the optical properties at different particle sizes. As shown in Figures 9a and 9b, for both winter and summer samples, the contribution of PAHs in the 0- to 3.3- μ m









Figure 7. The average UV-visible absorbance spectra of MSM and the calculated UV-visible absorbance spectra of the selected PAHs (a and b) and the relative contributions of the selected PAHs to the total light absorption by MSM (c and d). MSM = methanol-soluble matter; PAH = polycyclic aromatic hydrocarbon.

particle size range to the light absorption of MSM at 430 nm is significantly larger than that of PAHs in the 3.3- to 10- μ m particle size range. This difference is because a higher PAH content tends to occur in samples with smaller particle sizes (Figure 2f). For the contribution of PAHs to the light absorption of MSM at 365 nm, there is no obvious variation with particle size. As shown in Figure 9c, for winter samples, the PAHs contributing to the FV of MSM with sizes of <3.3 μ m are also significantly larger than those with a 3.3- to 10- μ m particle size range. For the summer fine particle samples, the PAHs have a larger contribution to FV for particle sizes of <0.43 μ m than that of other particle sizes, which is due to the higher content of PAHs. However, the contribution of particles with sizes of 0.43–1.1 μ m decreases, and the contribution of larger particles is higher, which is contrary to the measured particle size distribution of PAHs, indicating that other substances may be the major contributors to the chromophores rather than the selected PAHs.

3.4. Optical Properties of Aerosol Extracts Associated With OC, WSOC, WISOC, EC, and PAHs

The correlations between the optical properties of the particulate samples and the OC, EC, and PAHs are explored (Figures S11 and S12). For the winter samples, the light absorption and FV of WSM are only weakly positively correlated with WSOC ($r \ge 0.57$, p < 0.05), indicating that only part of the organic matter in the WSOC is composed of chromophores, including organic matter such as humic-like substances (HULIS) in WSM. Chen, Ikemori, and Mochida (2016) have reported that most of the light absorption in WSOC is contributed by HULIS but that the OC in HULIS only accounts for approximately half of the WSOC. In contrast, the light absorption and FV of MSM are positively correlated with WISOC ($r \ge 0.92$, p < 0.01), indicating that most WISOC contributes to the optical properties. The correlation between the Abs₃₆₅ and FV values of WSM and WISOC in summer (r = 0.76, p < 0.01) is better than that in winter, while the correlation between the Abs₃₆₅ and FV values of MSM and WISOC in summer (r < 0.49, p > 0.05) is obviously weaker than that in winter. Therefore, in summer samples, the water-insoluble chromophores may be photolyzed, while the water-soluble chromophores include secondary generation particles.





Figure 8. The average EEMs of MSM (a and b), the calculated EEMs of the selected PAHs (c and d), and the relative contributions of the selected PAHs to the EEMs by MSM (e and f). The color columns in the panels (a–d) and (e–f) represent the fluorescence intensity (RU) and the relative contributions of the selected PAHs to the total fluorescence intensity by MSM (%), respectively. MSM = methanol-soluble matter; EEM = excitation-emission matrix; PAH = polycyclic aromatic hydrocarbon.

The Abs₃₆₅ and FV values of both WSM and MSM are significantly positively correlated with the concentration of PAHs (r > 0.77, p < 0.01; Figure S12), indicating that the light-absorbing substances or chromophores in the PM samples in this study are most likely contributed by incomplete combustion sources. This result is similar to the conclusions of Huang et al. (2018), who found a significant positive correlation between the light absorption of PM2.5 and eighteen parent PAHs and carbonyl-OPAHs measured in Xi'an. The correlations between the optical properties of WSM and MSM with PAHs in winter samples are better than those in summer samples, indicating that the source of winter chromophores is similar to the source of PAHs, while the summer chromophores may be partially formed by secondary processes. Although we found that the optical properties of the samples are significantly correlated with PAHs, no EC-related properties were found (Figures S6 and S7). Thus, the main source/formation mechanisms of BrC/PAHs and EC may be different. In this study, EC is mainly distributed in the range of less than 0.43 µm, which is significantly different from the coal combustion emission characteristics reported in the literature (Yang et al., 2018), indicating that EC may originate from a mixture of sources, including vehicle exhaust and coal combustion, while both the PAHs and chromophores in atmospheric particulates may be mainly from coal combustion in Linfen. Moreover, the contributions of coal combustion to atmospheric PAHs and chromophores are greater in winter than in summer. Sun et al. (2017) have confirmed that coal combustion can emit abundant BrC, and the





Aerodynamic diameter (µm)

Figure 9. Size-resolved contributions of the selected PAHs to the total light absorption (a and b) and fluorescence volume (Ex: 200–450 nm and Em: 250–600 nm) (c) for MSM in summer (blue) and winter (yellow). MSM = methanol-soluble matter; PAH = polycyclic aromatic hydrocarbon.

light absorption by BrC accounts for more than a quarter of the total absorption by particulates derived from residential coal burning. In addition, the results of EEM and PARAFAC analysis also suggest that BrC in the samples of this study is unlikely to be mainly from BBOA (discussed in section 3.5).

This study found that the fluorescence intensity of PM is significantly positively correlated with the absorbance (r > 0.88, p < 0.01; Figures S6 and S7), which is consistent with the basic principle of fluorescence emission of a substance. However, the light-absorbing substances in atmospheric particulate samples are not necessarily all fluorescent, such as nitrophenolic compounds, which are a type of BrC commonly found in atmospheric particulates (Zhang, Lin, et al., 2013). We separately measured the light absorption and fluorescence properties of several nitrophenol standards, and the results showed strong light absorption properties, but no strong fluorescence signal was observed (the results are not shown here). Therefore, we expected that a majority of light-absorbing substances in the studied aerosols have fluorescent properties, and this result also ensures the advantage of identifying the species and sources of BrC by the EEM method. In addition, this study also found that the correlation between light absorption and fluorescence properties for winter samples is related to particle size (Figure S6). The scatter plots of light absorption and fluorescence properties for particle sizes of <0.43 and 0.43–10 μ m are significantly different, indicating that the chromophore species are significantly different.

3.5. PARAFAC Components and Size Distributions

To investigate the types of chromophores in the samples, as well as the differences in the types and contents of chromophores in different seasons, different polar extracts, and different particle sizes, this study successfully separated five fluorescence components from the EEM data using the PARAFAC method, and the results are shown in Figure 10. Based on the maximum excitation/emission wavelength of these five fluorescent components and literature reports (Chen, Ikemori, & Mochida, 2016, Chen, Miyazaki, et al., 2016, Yu et al., 2015), we defined C1 as the HULIS-1 component (Ex. = 255 nm, Em. = 415 nm), C2 as a tryptophan-like component (Ex. = 220 nm, Em. = 340 nm), C3 as the HULIS-2 component (Ex. = 225 nm, Em.

100





Figure 10. The PARAFAC model-resolved EEM components (C1, C2, C3, C4, and C5) for all of the aerosol extracts (n = 396) with the solvents water and methanol and extracted from different particle size samples.

= 385 nm), C4 as the tyrosine-like component (Ex. = 210 nm, Em. = 300 nm), and C5 as the amino acid-like component (Ex. = 250 nm, Em. = 355 nm). Because there is currently no special chemical structure corresponding to the chromophores in atmospheric organic aerosols, it is impossible to chemically define different types of chromophores. Therefore, the naming scheme does not imply that the chromophore is composed of the given substance but indicates that they have similar fluorescent properties. For example, C2 and C4 were tryptophan-like and tyrosine-like chromophores, respectively. However, Chen, Miyazaki, et al. (2016) showed that tryptophan-like and tyrosine-like components were not related to amino acids and N-containing ion fragments and speculated that the chromophore groups might be partly composed of phenolic compounds. The larger emission wavelengths of the HULIS chromophores imply that they originate from large conjugated systems, possibly highly aromatic conjugated structures containing heteroatoms (Chen, Ikemori, Higo, et al., 2016).

As shown in Figure 11, the relative amounts of the various chromophore components in the sample differ among the different seasons, particle sizes, and polarities of the extracts. The HULIS-1 and amino acid-like components are the most abundant chromophores in all samples, with average relative contents of 38% and 31%, respectively. The tyrosine-like component is the least abundant chromophore, with an average content of only 4% in all samples. The relative contents of chromophores in the samples vary seasonally. The average contents of the HULIS-1, HULIS-2, and amino acid-like components are 33%, 17%, and 34%, respectively, in winter and 71%, 4%, and 10%, respectively, in summer. Chen, Miyazaki, et al. (2016) noted that the HULIS-1 and HULIS-2 components represent high-oxidation and low-oxidation chromophores, respectively. Therefore, the increase in HULIS-1 and the decrease in HULIS-2 in summer samples may be related to the photochemical transformation of chromophores. We hypothesize that in summer, HULIS-1 is generated secondarily, while the HULIS-2 and amino acid-like components are oxidized and decomposed or converted into HULIS-1 or other types of chromophores. In addition, the fluorescent region of HULIS-1 has been associated with hydrophilic chromophore material (Chen, Ikemori, Higo, et al., 2016 and Chen, Miyazaki, et al., 2016), and the content of HULIS in summer samples is significantly higher than that in winter samples, indicating that hydrophilic chromophores might be generated in summer, consistent with the above conclusions. There is a slight difference in the average relative content of chromophores in extracts with different polarities for the atmospheric particulate samples. The HULIS-1 content (39%) in MSM is slightly higher than that in WSM (30%), while the HULIS-2 (15%) and tryptophan-like component (11%) contents in MSM are slightly





Figure 11. Size-resolved distributions of the excitation-emission matrix components for winter samples (a and e) and summer samples (b and f) of water-soluble matter and for winter samples (c and g) and summer samples (d and h) of methanol-soluble matter.

lower than those in WSM (21% and 16% for the HULIS-2 and tryptophan-like components, respectively). Similarly, Chen, Ikemori, and Mochida (2016) also found that a HULIS component (similar to HULIS-1 in this study) and a tryptophan-like component were abundant in the water-insoluble and water-soluble components of total suspended particle, respectively.

The relative content of various chromophores in samples with different particle sizes is also different, as shown in Figure 11. First, HULIS-1 tends to exist in small particles, except that the MSM component exhibits bimodal characteristics in winter. (One peak corresponds to the smallest particle sizes of $<0.43 \mu m$, and the other is in the range of 3.3–4.7 µm.) Second, the abundance of tryptophan-like and tyrosine-like components tends to increase with increasing particle size, especially when the particle size is approximately $3.3 \,\mu m$. These two chromophore types may be derived from bioaerosols. Previous studies have shown that large particles contain more bioaerosols, such as bacteria and fungi, than small particles (Li et al., 2011; Rathnayake et al., 2017), which is consistent with the results of this study. Third, the abundance of HULIS-2 chromophores in WSM samples increases slightly with increasing particle size (with an average content of 9%), while the HULIS-2 chromophores in MSM samples are primarily present in particles $<3.3 \mu m$ in summer (with an average of approximately 15%), and the content is very low in the large-particle samples in summer and in all samples in winter. Therefore, the HULIS-2 chromophores may be susceptible to photolysis; for example, these chromophores may be photochemically transformed to the HULIS-1 chromophore (Chen, Miyazaki, et al., 2016). Fourth, the C5 component (amino acid-like species) varies with particle size among different seasons and solution polarities. In summer, the relative content of the amino acid-like component in both WSM and MSM samples increases with increasing particle size (Figures 11f and 11h). In contrast, in winter, the amino acid-like components in the WSM samples decrease with increasing particle size (Figure 11e), while variation in the MSM samples is not obvious (Figure 11g).

The results of this study show that the species and composition of chromophores in different particle sizes and seasons were different, which reflects differences in chemical compositions and/or sources. Generally, biomass combustion emissions are an important source of atmospheric chromophores. However, the results of this study show that the excitation wavelength of the HULIS chromophores in this study (Ex. = 255 and 225 nm) is significantly smaller than that of the HULIS chromophores originating from BBOA (Ex. = 300 nm). It is assumed that the chromophores in this study are unlikely contributed mostly by biomass combustion. According to the characteristics and current situation of regional air pollution in Linfen, the main source of chromophores in atmospheric particles is speculated to be coal combustion (Wang et al., 2017). Coal combustion reportedly produces abundant BrC (Sun et al., 2017).



4. Conclusions

This study reports the size-resolved characterization of the chromophores in atmospheric PM in Linfen, China. The total light absorption (Abs) and FV of particles of different sizes was less than 10 μ m, and the MAE and NFV based on the mass concentration of the OC in extracts varied with the particle size. The results reveal that the smaller the particle size was, the stronger the absorbance and the fluorescence of extracted water-soluble and water-insoluble chromophores, indicating that small particles make larger contributions than large particles to the light absorption and photochemical reactions. Furthermore, the light absorption and fluorescence properties of the water-insoluble chromophores are stronger than those of the water-soluble chromophores in both winter and summer and among the different particle sizes, and the total Abs and FV values of water-insoluble chromophores from particles of different sizes and with different polarities to light absorption and photochemical reactions should be considered in future atmospheric models.

This study quantitatively evaluated the contribution of PAHs to the light absorption and fluorescence properties of water-insoluble components. The average contribution of the seven selected PAHs to the total light absorption and fluorescence values of the samples was <3%, indicating that other substances have a greater impact on the properties of MSM than the selected PAHs. The total concentration of the seven selected PAHs is strongly positively correlated with the light absorption and fluorescence intensity of both the water-soluble and water-insoluble components. Therefore, the chromophores in the samples are most likely derived from an incomplete combustion source. However, this study did not find that the optical properties of PM samples are positively related to EC, another tracer of incomplete combustion sources. Consequently, the main source of chromophore substances and PAHs is different from the main contribution sources of EC, and the main source of chromophores and PAHs is speculated to be coal combustion.

This study is the first to report the particle size distribution characteristics and contents of chromophore types in Linfen, a typical coal-burning area. The results show that the contents of the five chromophores obtained by PARAFAC analysis are different not only between water-soluble and water-insoluble components but also among different seasons, and the relative contents of different chromophores vary significantly with particle size. The HULIS-1 and amino acid-like components are the most abundant chromophores in all samples, whereas the tyrosine-like component are the least abundant chromophores. HULIS-1, which may be related to the formation of secondary aerosols, tends to be present in small particles, while tryptophan-like and tyrosine-like components, which may be derived from bioaerosols, tend to increase in abundance with increasing particle size. This study demonstrates that EEM analysis and PARAFAC analysis are very effective approaches for studying the chemical compositions and sources of chromophores in the atmosphere. Moreover, the results of this study indicate that the fluorescence intensity of PM is dependent on absorbance. This result also allows the scientific identification of BrC species and sources by EEM, and the compositional information on the chromophores provided by EEM is more than that provided by UV-Vis spectra. We propose that the EEM method should be extended and further studied for determining the types, chemical structures, formation processes, and sources of chromophores. At present, the bottleneck in the application of EEM in the study of atmospheric chromophores still lies in the lack of corresponding information on the types, structures, and sources of EEM components and specific compounds. We suggest that this scientific problem should be further studied and that the EEM method be extensively applied to study the source and formation mechanism of atmospheric chromophores.

Acknowledgments

This study was financially supported by the National Key R&D Program of China (grant no. 2017YFC0212704), the National Natural Science Foundation of China (grant numbers 41761144056, 41877354, and 41703102), and the Provincial Natural Science Foundation of Jiangsu (grant no. BK20180040). All the data used in this paper can be downloaded via https://pan.baidu.com/ s/10Q0EBgJ5fowSupHU3Mg9dQ (code: 24iy).

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