



Optical characteristics and source apportionment of brown carbon in winter PM_{2.5} over Yulin in Northern China

Yali Lei^{a,b}, Zhenxing Shen^{a,b,*}, Qiyuan Wang^b, Tian Zhang^a, Junji Cao^b, Jian Sun^a, Qian Zhang^a, Linqing Wang^a, Hongmei Xu^a, Jie Tian^a, Jiamin Wu^a

^a Department of Environmental Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, China

^b Key Lab of Aerosol Chemistry & Physics, SKLLQG, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710049, China

ARTICLE INFO

Keywords:

Brown carbon

Coal combustion

Source apportionment

ABSTRACT

In this study, daily PM_{2.5} samples were collected at an urban site in Yulin of Northern China during a winter season. Eight carbon fractions, 13 kinds of polycyclic aromatic hydrocarbons (PAHs), and nine water-soluble ions in PM_{2.5} were measured. The light-absorption characteristics of brown carbon (BrC) both in water and in methanol extracts were evaluated and quantified. The total quantified PAHs exhibited high concentrations ($228.4 \pm 52.6 \text{ ng m}^{-3}$), contributing 0.2% of the PM_{2.5} mass. High indeno[1,2,3-*cd*]pyrene/(indeno[1,2,3-*cd*]pyrene + benzo[ghi]-perylene) ratio but low $\text{NO}_3^-/\text{SO}_4^{2-}$ ratio revealed the important contribution of coal combustion to PM_{2.5}. The absorption coefficient (b_{abs}) for methanol extracts measured at 365 nm averaged $27.5 \pm 12.0 \text{ Mm}^{-1}$. Light absorption by methanol extracts exhibited strong wavelength dependence, with an average absorption Ångström exponent of 5.2 in the 330–400 nm range. The mass absorption cross section (for methanol extracts averaged $1.4 \pm 0.4 \text{ m}^2 \text{ g}^{-1}$ by normalizing b_{abs} measured at 365 nm to organic carbon mass. A relatively strong positive relationship between $b_{\text{abs, methanol}}$ and benzo[a]pyrene as well as with six carbon fractions indicated the important contribution of coal burning to BrC. Source apportionment based on the positive matrix factorization receptor model and multiple linear regression showed that residential coal combustion accounted for 37.4% of $b_{\text{abs365, methanol}}$. The estimated relative radiative forcing by methanol-soluble organic carbon relative to elemental carbon was 36.9% at 300–400 nm.

1. Introduction

Light-absorbing aerosols have drawn growing attention in recent years because of their important role in radiative forcing and visibility impairment (Gelencser et al., 2003; Lukacs et al., 2007; Barnard et al., 2008; Hecobian et al., 2010; Srinivas and Sarin, 2014). Aerosol light-absorbing components in the atmosphere can be classified into black carbon (BC), mineral dust and some organic carbon (named brown carbon, BrC) (Wan et al., 2016; Wang et al., 2016a; Park and Son, 2017). BC is the most potent absorber in the visible wavelengths (Bond, 2001; Bond et al., 2013; Lihavainen et al., 2017), whereas BrC shows prominent absorption in the near-UV region (Hecobian et al., 2010; Lack et al., 2012; Liu et al., 2014). BrC accounts for 20%–50% of light absorption at short wavelengths, indicating the importance of BrC in the ultraviolet (UV) region (Kirchstetter and Thatcher, 2012; Feng et al., 2013; Mohr et al., 2013; Jo et al., 2015). These modeling studies suffered from substantial uncertainties, such as sources, optical properties, and chemical transformations of BrC.

BrC can absorb light based on a variety of chemical structures like nitrated and polycyclic aromatics, phenols, humic-like substances (HULIS), and biopolymers (Jacobson, 1999; Hoffer et al., 2006; Desyaterik et al., 2013; Sun et al., 2013; Teich et al., 2017). Main sources of BrC can include combustion emissions (such as biomass burning and biofuel burning) (Bond, 2001; Kirchstetter et al., 2004), HULIS from multiple-phase actions, and secondary organic carbon (SOC) from photochemical oxidation or aqueous reaction processes (Chakrabarty et al., 2010; Hecobian et al., 2010; Cheng et al., 2016; Shen et al., 2017a). Accordingly, the variety of molecular compositions of BrC and its mixing state with other substances make it challenging to research BrC in particulate matter (PM) (Alexander et al., 2008). Solvent extraction (using water or organic solvents) can separate a substantial fraction of organic carbon from PM (Chen and Bond, 2010; Zhang et al., 2011). As a result, the popular optical measurement method of BrC determines extracts absorption (Hecobian et al., 2010; Cheng et al., 2016). For example, Hoffer et al. (2006) generated absorption spectra of the HULIS isolated from biomass-burning source

* Corresponding author at: Department of Environmental Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, China.
E-mail address: zxshen@mail.xjtu.edu.cn (Z. Shen).

samples collected in the Amazon basin and estimated that HULIS contributed 6.4%–8.6% of the entire solar spectrum absorption. In another study conducted in Atlanta and reported by Liu et al. (2013), absorption by BrC was calculated using Mie theory based on size-resolved measurements of water-soluble organic carbon (WSOC) absorption spectra, and it was predicted that BrC contributed 20%–40% of total aerosol light absorption at 350 nm. The optical properties of BrC were also observed at an urban site in Gwangju, Korea, and the contribution of primary biomass burning accounted 26.1% to water extract BrC absorption (Park et al., 2018). Extensive experimental data [e.g., absorption coefficient (b_{abs}), Ångström exponent (AAE), and mass absorption cross section (MAC)] are essential to evaluate light absorption by BrC (Liu et al., 2013; Shen et al., 2017a; Yuan et al., 2016; Park et al., 2018).

A large number of studies have been conducted in China investigating PM_{2.5} chemical composition, source apportionment, and optical properties, as reviewed in Tao et al. (2017). Most of the studies on optical properties of PM_{2.5} focused on black carbon (BC) and secondary inorganic species (sulfate, nitrate, and ammonium). The studies on optical properties of BrC were limited in China (such as Cheng et al., 2015; Cheng et al., 2016; Shen et al., 2017a, 2017b). Yulin (36.95°–39.58°N, 107.46°–111.25°E), with a population of ~3.36 million and an area of ~43,600 km², is located in the transition zone between the Chinese Loess Plateau and the Mu Us Desert, Shaanxi Province. This area is a national energy and chemical industrial center, and coal combustion is a big air-pollution problem in Yulin (Cao et al., 2012a; Guo et al., 2015). In addition, most previous studies usually illustrated that biomass burning was a major contributor to BrC (Yan et al., 2015; Shen et al., 2017b), and few studies have addressed the important contribution of coal burning to BrC and its radiative forcing. As a result, the objectives of the present study are 1) to investigate chemical characteristics of PM_{2.5} in Yulin, 2) to reveal the optical characteristics and sources of solvent-extracted BrC in PM_{2.5}, and 3) to estimate the radiative forcing contributions of BrC extracts from (WSOC) and methanol soluble organic carbon (MSOC).

2. Methodology

2.1. Sample collection

Sampling was conducted on the roof of the 12-m high building of the environmental monitoring station, located in a commercial-residential-traffic mixed urban site in Yulin (Fig. 1). Daily PM_{2.5} samples (24-h starting at 9,30 am) were collected on 47-mm quartz microfiber filters (Whatman, Maidstone, UK) from 19 December 2015 to 1 January 2016. (Fig. 1) using a 5 L min⁻¹ mini-volume sampler (Airmetrics, Springfield, OR, USA). The quartz filters were pre-heated at 800 °C for 3 h to remove any residual carbon before using. The detail description of filters weighting before and after sampling can be found in Shen et al. (2009). Additional quality assurance and quality control procedures were described in Cao et al. (2012a) and Shen et al. (2017a).

2.2. Chemical analysis

PM_{2.5} organic carbon (OC) and elemental carbon (EC) were determined with a DRI Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, USA) following the improved TOR protocol (Chow et al., 2004). The IMPROVE_A (Interagency Monitoring of Protected Visual Environments) protocol produces four OC fractions (OC1, OC2, OC3, and OC4 at 140 °C, 180 °C, 480 °C, and 580 °C respectively, in a 100% He atmosphere); a pyrolyzed carbon fraction (OP, determined when reflected or transmitted laser light attained its original intensity after O₂ was added to the analysis atmosphere); and three EC fractions (EC1, EC2, and EC3 in a 98% He/2% O₂ atmosphere at 580 °C, 740 °C, and 840 °C respectively) (Chow et al., 2004). Details of quality assurance and control procedures were described in Cao et al.

(2005).

Water soluble inorganic ions (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, F⁻, Cl⁻, NO₃⁻, and SO₄²⁻) levels were determined using an ion chromatograph (IC, Dionex 500, Dionex Corp., Sunnyvale, CA, USA). Anions were analyzed using an ASII-HC column (Dionex Corp.) and 20 mM potassium hydroxide as the eluent. Cations were determined using a CS12A column (Dionex Corp.) with 20 mM methane sulfonic acid as the eluent. A detailed description of the ion analysis method used in this study can be found in Shen et al. (2008, 2009).

Concentrations of 13 kinds of priority-controlled polycyclic aromatic hydrocarbon (PAHs) as defined by the United States EPA were determined: fluorine (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flua), pyrene (Pyr), benzo[k]fluoranthene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IP), dibenzo[a,h]anthracene (dBahA), and benzo[ghi]perylene (BghiP) (Supelco, American Chemical Society (ACS) standard grade, purity from 93.4% to 99.9%). PAHs were analyzed using gas chromatography with mass-selective detection (GC–MS). The chromatographic conditions were as follows: injector temperature 290 °C and detector temperature 250 °C. The temperature ramp was an initial oven temperature of 50 °C maintained for 2 min, increased at 5 °C/min to 280 °C, and then increased at 3 °C/min to a maximum of 300 °C for 10 min. The detailed pretreatment process and quality assurance and quality control can be found in Shen et al. (2017b).

2.3. Optical properties of methanol and water extracts

Light absorption spectra of the methanol and water extracts were measured over the wavelength range of 190–1100 nm using a UV–Vis spectrophotometer (UV-6100 s, MAPADA, Shanghai, China), following the method developed by Hecobian et al. (2010). The extraction methods were detailed described in Shen et al. (2017b). b_{abs} of water and methanol extracts of PM_{2.5} samples can be calculated as:

$$b_{\text{abs}\lambda, \text{water/methanol}} = (A_{\lambda, \text{water/methanol}} - A_{700, \text{water/methanol}}) * (V_{\text{ext}} * \text{portions}) * \ln(10) / (V_{\text{aero}} * L) \quad (1)$$

where b_{abs} is expressed in units of Mm⁻¹ (or 10⁻⁶ m⁻¹). A_{λ} and A_{700} correspond to measured absorbances at the specified λ and 700 nm respectively. V_{ext} refers to the volume of the solvent extract (50 mL) for different portions of filter. V_{aero} represents sampling volume, and L is the path length of the cell (10 cm). The reference wavelength λ is chosen as 365 nm to represent light absorption of organic aerosol in order to be consistent with previous studies, and avoid light-absorbing disturbance by other substances (e.g., nitrate) (Liu et al., 2013; Cheng et al., 2016).

The wavelength-dependent AAE and b_{abs} of BrC in the solvent extracts can be described following Hecobian et al. (2010) as:

$$b_{\text{abs}\lambda, \text{water/methanol}} = K * \lambda^{-\text{AAE water/methanol}} \quad (2)$$

where K is a constant and λ denotes the wavelength of BrC. In this study, AAE was calculated by linear regression fitting to log b_{abs} vs. log λ in the 330–400 nm wavelength range.

According to Liu et al. (2013) and Shen et al. (2017b), ambient OC concentrations for the methanol extracts was used to calculate MAC_{365, methanol} based on the following equation:

$$\text{MAC}_{\lambda, \text{methanol}} = b_{\text{abs}\lambda, \text{methanol}} / \text{OC} \quad (3)$$

2.4. Source apportionment model for PM_{2.5}

Positive matrix factorization (PMF) is a bilinear factor model (Paatero and Tapper, 1994) that has been widely used in source apportionment studies (Cao et al., 2012b; Tao et al., 2014; Xiao et al., 2014; Wang et al., 2016b). The concept of PMF has been described in

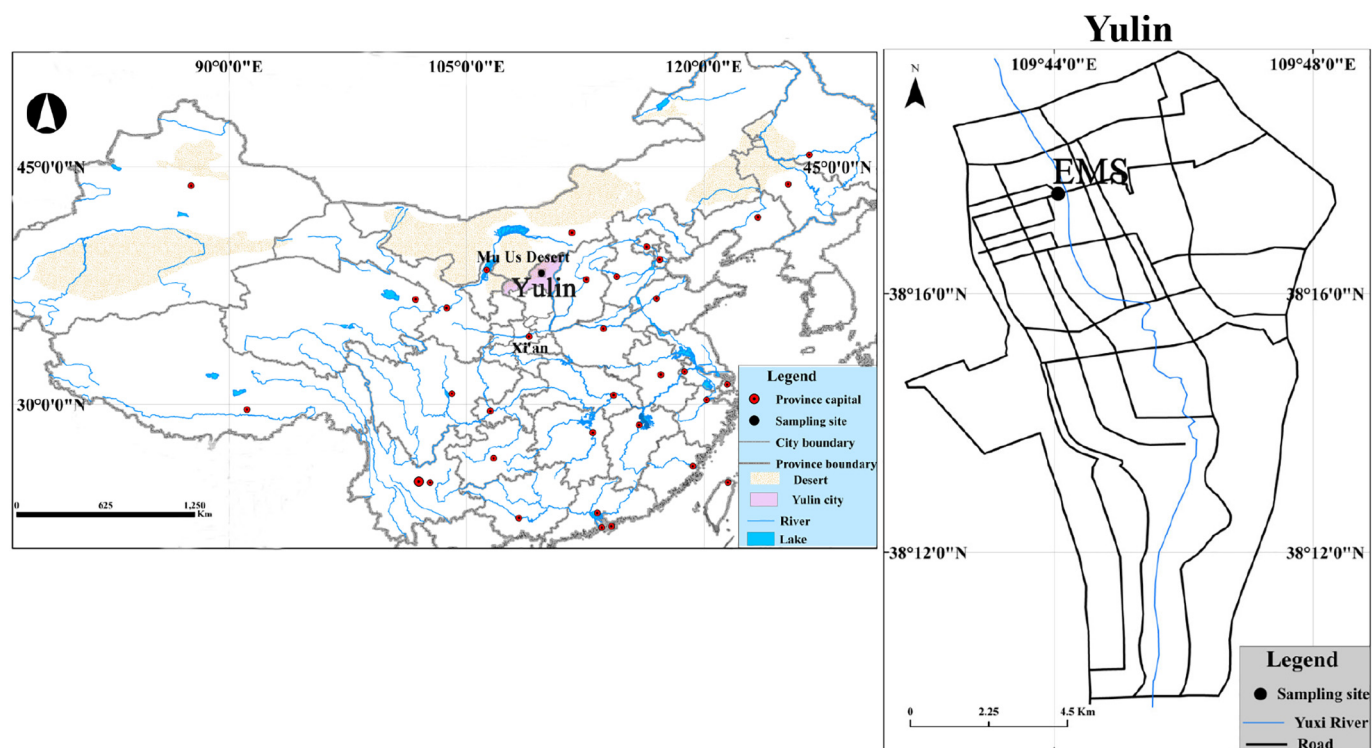


Fig. 1. Location of the monitoring site and surrounding region.

detail by Zhou et al. (2017). Water-soluble inorganic ions (NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , and SO_4^{2-}), eight carbon fractions (OC1, OC2, OC3, OC4, EC1, EC2, EC3, and OP), and PAHs (Flua, Pyr, BbF, BkFIA, and BaP) were used as data inputs. The PMF model was run multiple times, extracting four to six factors, and each run was initialized with different starting points (changing the seed value from 1 to 20). The discussion that follows is based on the five-factor model resulting from PMF analyses.

3. $b_{\text{abs}365}$, methanol source apportionment

To investigate the contributions of each emission source to $b_{\text{abs}365, \text{methanol}}$, a multivariate linear regression model was constructed.

The relationships between $b_{\text{abs}365, \text{methanol}}$ and each emission source can be described as:

$$b_{\text{abs}365, \text{methanol}} = B + \sum_{i,j=1}^n A_i \times [X_{ij}] \quad (4)$$

where the quantities in brackets $[X_{ij}]$ represent the contributions of the i -th emission source (units: Mm^{-1}) on the j -th day; A_i and B represent the regression coefficient and random error respectively; $A_i \times [X_{ij}]$ represents the predicted values of $b_{\text{abs}365, \text{methanol}}$ from the i -th emission source.

3.1. Radiative forcing of WSOC and MSOC relative to EC

This study used a simple model to evaluate the solar energy absorbed by WSOC and MSOC (integrated over a broad wavelength range between 300 and 2500 nm) relative to EC. The wavelength-dependent solar emission flux ($I_0(\lambda)$) was approximated using the clear-sky Air Mass 1 Global Horizontal (AM1GH) solar irradiance model proposed by Levinson et al. (2010).

The fraction of solar energy absorbed by WSOC or MSOC relative to EC (f) can be calculated as follows:

$$f = \frac{\int I_0(\lambda) \left\{ 1 - e^{-\text{MAC}_{365} \left(\frac{365}{\lambda} \right)^{\text{AAE}_{\text{WSOC}/\text{MSOC}} \times c_{\text{WSOC}/\text{MSOC}} \times h_{\text{ABL}}} \right\} d\lambda}{\int I_0(\lambda) \left\{ 1 - e^{-\text{MAC}_{632} \left(\frac{632}{\lambda} \right)^{\text{AAE}_{\text{EC}} \times c_{\text{EC}} \times h_{\text{ABL}}} \right\} d\lambda} \quad (5)$$

where λ is the wavelength, MAC_{365} is the mass absorption cross section for WSOC and MSOC at 365 nm, MAC_{632} is the mass absorption cross section for EC at 632 nm, and h_{ABL} is the height of the atmospheric boundary layer. For the current simplistic model, $\text{MAC}_{632} = 8.45 \pm 1.71 \text{ m}^2 \text{ g}^{-1}$ as reported by Cheng et al. (2011), and the AAE for EC was set to one. h_{ABL} was set to 1000 m because it was found to have little influence on the computed ratio in the 200–3000 m range (Kirillova et al., 2014). AAE for MSOC and WSOC were measured at 330–400 nm. Solar light is well approximated by the AM1GH, and no effects of scattering (by aerosols or cloud droplets) are available.

4. Results and discussion

4.1. General description of the chemical composition of winter $\text{PM}_{2.5}$ over Yulin

Table 1 summarizes $\text{PM}_{2.5}$ levels, carbonaceous components, water-soluble ions, and PAHs in Yulin. Winter average $\text{PM}_{2.5}$ was $110.6 \mu\text{g m}^{-3}$, which exceeded the Class II National Air Quality Standards of China ($75 \mu\text{g m}^{-3}$). Higher winter $\text{PM}_{2.5}$ levels in Yulin were also found by Cao et al. (2012a). Daily average organic matter (OM, estimated as $1.6 \times \text{OC}$, Turpin and Lim, 2001) was $33.9 \pm 18.5 \mu\text{g m}^{-3}$ during the sampling period, accounting for 33.7% of $\text{PM}_{2.5}$ mass. The mean value of EC in winter was $6.4 \pm 3.4 \mu\text{g m}^{-3}$ and contributed about ~6.6% of $\text{PM}_{2.5}$ mass. A high OC/EC ratio (3.2) was observed during this study, which was very close to the OC/EC ratio of coal-combustion source profiles (2.7, Watson et al., 2001). In addition, high sulfate concentrations, but low nitrate concentrations (with a low $\text{NO}_3^-/\text{SO}_4^{2-}$ ratio of 0.3 ± 0.2) were also observed, which further demonstrated that coal combustion can be expected to be one of the major sources of winter $\text{PM}_{2.5}$ over Yulin (Arimoto et al.,

Table 1

Optical properties and mass concentrations of chemical species for PM_{2.5} samples during winter in Yulin.

	Average	Standard deviation
PM _{2.5} (μg m ⁻³)	110.6	73.9
TC (μg m ⁻³)	27.3	15.2
OM (μg m ⁻³)	33.9	18.5
OC (μg m ⁻³)	21.2	11.5
EC (μg m ⁻³)	6.4	3.4
OC/EC	3.2	0.5
Total Ions (μg m ⁻³)	24.6	23.8
K ⁺ (μg m ⁻³)	0.5	0.6
NO ₃ ⁻ (μg m ⁻³)	2.8	4.1
SO ₄ ²⁻ (μg m ⁻³)	10.8	11.0
NO ₃ ⁻ /SO ₄ ²⁻	0.3	0.2
Total PAH (ng m ⁻³)	228.4	52.6
BaP (ng m ⁻³)	19.0	6.6
IP (ng m ⁻³)	18.2	5.0
BghiP (ng m ⁻³)	14.4	5.1
dBahA (ng m ⁻³)	32.5	9.4
IP/(IP + BghiP)	0.6	0.1
b _{abs,water} (Mm ⁻¹)	8.9	4.9
AAE _{water}	5.2	0.8
b _{abs, methanol} (Mm ⁻¹)	27.5	12.0
AAE _{methanol}	4.9	1.2
MAC _{methanol} (m ² g ⁻¹)	1.4	0.4

2004).

The total quantified PAHs concentrations in winter ranged from 165.5 to 386.0 ng m⁻³ and averaged 228.4 ng m⁻³, contributing 0.2% of the PM_{2.5} mass. It was noted that dBahA was the most abundant species among the 13 PAHs, accounting for 14.5% of total measured PAHs. The PAH ratio is popular and widely used to identify sources. A previous study reported values for IP/(IP + BghiP) of 0.18, 0.37, and 0.56 for gasoline, diesel, and coal combustion respectively (Duan et al., 2007). In the present study, the IP/(IP + BghiP) ratio was in the 0.40–0.67 range, indicating that coal burning was the dominant contributor to PAHs. The abundance of BaP and IP also supported the important contribution of coal combustion.

4.2. Light absorption by water and methanol extracts

In this study, b_{abs} of water and methanol extracts were primarily investigated at a wavelength of 365 nm, and the results were compared with those from previous studies. Daily variation of b_{abs365,water} in winter exhibited a similar pattern to b_{abs365, methanol} with a b_{abs365, methanol} to b_{abs365,water} ratio of ~3.4, demonstrating that methanol extract was more effective in measuring BrC optical properties than water extract. Previous studies had suggested that b_{abs365, methanol} was always greater than b_{abs365,water} (Liu et al., 2013; Zhang et al., 2013). These results also highlighted that water-insoluble organic matter dominated in BrC compounds. Chen and Bond (2010) suggested that these strongly light-absorbing methanol-soluble components are likely large-molecular-weight PAHs, such as quinones from coal combustion. The b_{abs365, methanol} to b_{abs365,water} ratio in Beijing was 2.5 (Cheng et al., 2016), which was slightly lower than in Yulin. In addition, the light-absorptive properties of solvent extracts might be different from those of ambient aerosols, and therefore it should be noted that solvent-extract b_{abs} was measured for aerosol solutions rather than airborne particles. This indicated that the optical properties of BrC could be greatly underestimated by studies using WSOC as BrC. b_{abs365, methanol} varied greatly from 10.9 to 53.7 Mm⁻¹ (Fig. 2), with an average of 27.5 ± 12.0 Mm⁻¹ (Table 1). b_{abs365, methanol} has been compared with other cities, such as Beijing (26.2 Mm⁻¹, Cheng et al., 2016), Xi'an (21.8 Mm⁻¹, Shen et al., 2017b) and Gwangju, Korea (7.1 Mm⁻¹, Park et al., 2018).

Fig. 3 shows daily variation of AAE_{water} and AAE_{methanol} (330–400 nm) in winter. AAE_{water} ranged from 3.9 to 7.2, with an

average of 5.2 ± 0.8 (Table 1), which covered aged and fresh SOC and primary sources (e.g., coal combustion, Yang et al., 2009). Similar results were reported in the Los Angeles Basin (Zhang et al., 2013), the southeastern United States (Hecobian et al., 2010), Beijing (Cheng et al., 2016), and Xi'an (Shen et al., 2017a). AAE_{methanol} varied from 3.1 to 7.4, with a mean of 4.9 ± 1.2. A similar result can be found in Gwangju, Korea by Park et al. (2018), in which AAE_{methanol} ranged from 4.3 to 5.7 with an average of 4.8. AAE_{methanol} values were somewhat lower than AAE_{water} except for ten of the sampling days, when methanol extracts had a distinctive absorption band at longer wavelengths. This should mainly reflect specific organic materials such as nitrogen-containing organic compounds (Bones et al., 2010; Laskin et al., 2014). On the basis of these studies, the optical sources of BrC in methanol extracts are discussed in this paper.

Winter mean MAC_{365, methanol} was 1.4 ± 0.4 m² g⁻¹, similar to the previous study measured in Gwangju, Korea of 1.3 ± 0.4 m² g⁻¹ (Park et al., 2018). If the MSOC to OC ratio is assumed to be 0.85 (Cheng et al., 2016), the corrected MAC_{365, methanol} value should be ~1.7 ± 0.5 m² g⁻¹. The value is a little higher than in Beijing (1.4 ± 0.3 m² g⁻¹), which was related to biomass burning and other primary emissions (Cheng et al., 2016). Zhang et al. (2013) illustrated that the corrected MAC_{365, methanol} measured in the Los Angeles Basin, an area characterized by anthropogenic emissions origin rather than biomass burning, was ~1.9 m² g⁻¹. The MAC_{365, methanol} level normalized by MSOC over Xi'an was 1.72 during winter, which is strongly related to biomass burning and coal combustion for heating as well as fresh SOC from aqueous reactions (Shen et al., 2017b). However, PM_{2.5} MAC_{365, methanol} was only 0.69 m² g⁻¹ during summer, which was influenced by aged SOC generated from photochemical reactions. Primary combustion emissions other than vehicle exhaust were limited (Shen et al., 2017b). Another study in Georgia, United States, where SOC was mainly influenced by biogenic emissions, also showed relatively low summer MAC (0.3 to 0.5 m² g⁻¹) (Liu et al., 2013; Zhang et al., 2013). Hence, high MAC_{365, methanol} should be strongly associated with primary combustion processes such as biomass burning and coal combustion, whereas low MAC_{365, methanol} should be associated with SOC, especially aged SOC.

4.3. Sources of BrC

Previous studies have documented that BrC can originate from both primary and secondary processes (Chakrabarty et al., 2010; Cheng et al., 2011; Hecobian et al., 2010; Shen et al., 2017b). To assess the sources of atmospheric BrC, primary organic carbon (POC) and SOC were estimated for the sampling days using an EC tracer method as in the following equation (Ram and Sarin, 2011):

$$SOC = OC_{tot} - EC \times (OC/EC)_{min} \quad (6)$$

$$POC = OC_{tot} - SOC \quad (7)$$

where OC_{tot} is total OC and (OC/EC)_{min} is the minimum OC/EC ratio observed during sampling in Yulin. The estimated POC concentrations ranged from 3.9 to 29.9 μg m⁻³, with an average of 14.5 μg m⁻³, contributing 69.5% of the total OC mass. The fractional contributions of SOC to OC varied from 15.3% to 59.3% (Av: 30.5 ± 12.1%). b_{abs365, methanol} showed positive correlations with POC (r = 0.91) and SOC (r = 0.85) (Fig. 4), indicating that the primary emissions contribution is greater than secondary formation in winter.

Nitrated aromatic compounds, PAHs, and benzaldehydes were found to be the most effective UV absorbers in terms of their imaginary refractive indices and absorption wavelengths (Jacobson, 1999). In the present study, 13 PAHs were determined to reveal the possible sources of BrC (Table S1). For example, high BaP levels came mainly from coal combustion (Sawicki, 1962); the IP abundance was a typical component of diesel vehicle emissions, and BghiP enrichment was an indicator of gasoline vehicle emissions (Guo et al., 2005). The relatively strong

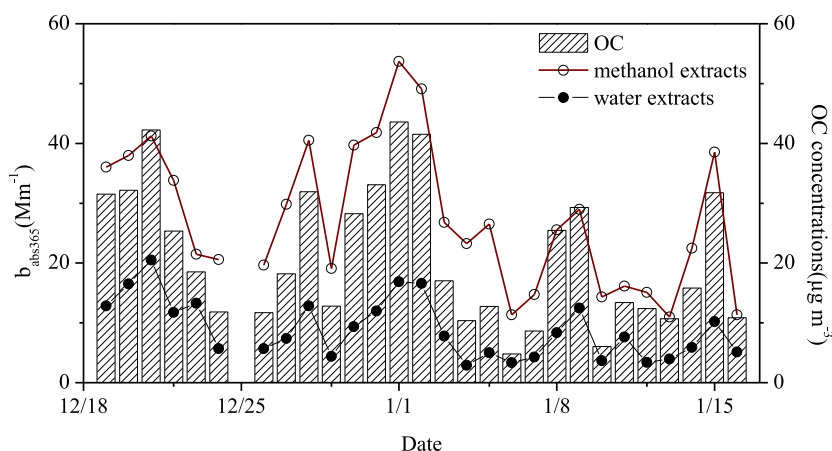


Fig. 2. Daily variations of OC, $b_{\text{abs}365}$ for water and methanol extracts.

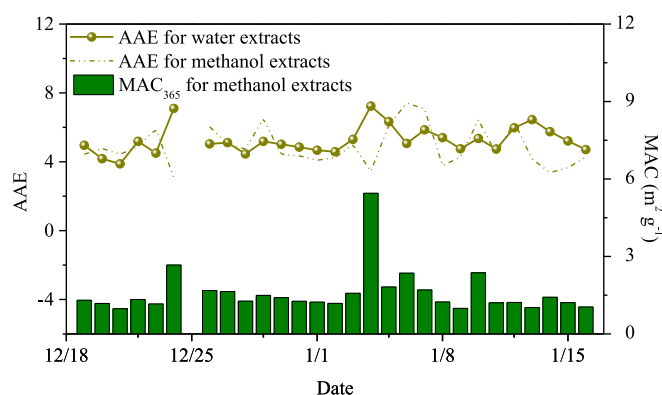


Fig. 3. Daily variations of MAC for methanol extracts and AAE for water and methanol extracts. AAE is calculated by linear regression fit to $\log b_{\text{abs}}$ vs. $\log \lambda$ in the wavelength range of 330–400 nm. MAC of the methanol extracts at a given wavelength is calculated as: $\text{MAC}_{\lambda, \text{methanol}} = b_{\text{abs} \lambda, \text{methanol}} / \text{OC}$.

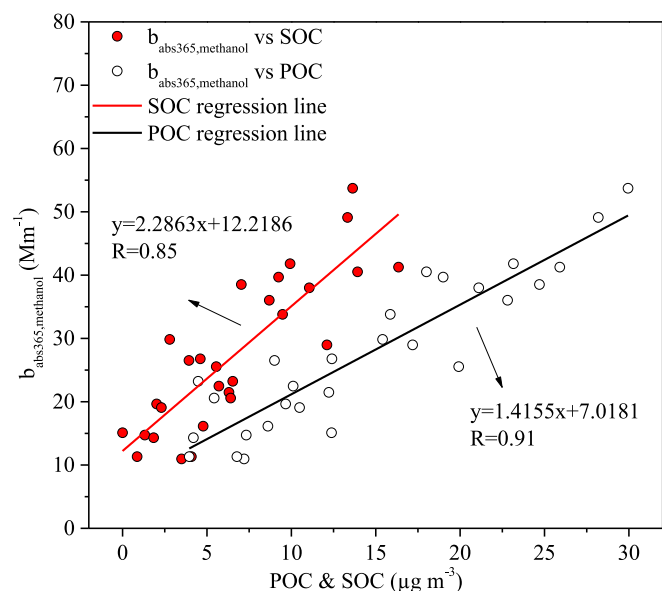


Fig. 4. A strong positive relationship between the abundance of POC & SOC and $b_{\text{abs}365, \text{methanol}}$.

positive relationship between $b_{\text{abs}, \text{methanol}}$ and BaP ($r = 0.67$) indicated the important contribution of coal burning to BrC. In contrast, the correlation coefficients between b_{abs} and IP ($r = 0.45$) or BghiP

($r = 0.32$) were lower than with BaP, supporting the conclusion that vehicle emissions were not an important contributor to BrC compared to coal combustion.

Previous studies illustrated that the BrC source contribution to light absorption were estimated with a multivariate linear regression approach (Zhou et al., 2017; Park et al., 2018). In this study, to investigate $b_{\text{abs}365, \text{methanol}}$ sources, a PMF model was first used to apportion $\text{PM}_{2.5}$ sources using data for the measured $\text{PM}_{2.5}$ chemical species. Then a multivariate linear regression model was used to investigate the contribution of each source to $b_{\text{abs}365, \text{methanol}}$. Five factors were identified from the PMF model and are presented in Fig. S1.

Factor 1 was characterized by Mg^{2+} , Ca^{2+} , K^{+} , and Cl^{-} , which were characteristic of fugitive dust (Shen et al., 2008; Zhang et al., 2014). Factor 2 loaded with sulfate and PAHs such as Flua and Pyr, representing emissions from industrial coal combustion (Huang et al., 2013; Shakeri et al., 2016). Traffic-related emissions were identified as Factor 3 was abundance of EC2, Ca^{2+} , Mg^{2+} , and PAHs (Flua, Pyr, BbF, BkFIA, and BaP) (Shakeri et al., 2016). Factor 4 loaded with NH_4^{+} , NO_3^{-} , and SO_4^{2-} , indicating a secondary formation source (Shen et al., 2010). Factor 5 had high loadings on eight carbon fractions and PAHs, which gave preliminary indications of emissions from combustion. In fact, Yulin is rich in coal resources and has few emissions from biomass burning (Guo et al., 2015). Therefore, Factor 5 was attributed to residential coal combustion. The contributions of the sources resulting from the PMF analyses were calculated by multiple regression of the G matrix (Paatero and Tapper, 1994) against the measured mass concentrations. Residential coal combustion contributed significantly to the detected $\text{PM}_{2.5}$ mass (36.9%), followed by industrial coal combustion (21.8%), secondary formation (19.3%), traffic-related emissions (11.7%), and fugitive dust (10.3%) (Fig. S2).

Fig. 5 shows the source contributions to $b_{\text{abs}365, \text{methanol}}$ obtained using a multivariate linear regression model. Because dust was not present in the solvent extract, fugitive dust and traffic-related emissions (including road dust) could not be investigated in the apportioning of $b_{\text{abs}365, \text{methanol}}$. Therefore, almost 53.5% of $b_{\text{abs}365, \text{methanol}}$ emissions were apportioned in this study, which indicated that the light absorption of methanol extracts could have arisen from other sources like bioaerosols or HULIS (Hoffer et al., 2006; Laskin et al., 2015). The $b_{\text{abs}365, \text{methanol}}$ of residential coal combustion was highest, with an average of $11.81 \pm 8.79 \text{ Mm}^{-1}$, accounting for 42.9% of total $b_{\text{abs}365, \text{methanol}}$. The $b_{\text{abs}365, \text{methanol}}$ values showed lesser contributions from secondary formation ($2.01 \pm 2.91 \text{ Mm}^{-1}$) and industrial coal combustion ($0.89 \pm 1.04 \text{ Mm}^{-1}$). It was inferred that residential coal burning was an important contributor to BrC emissions in Yulin.

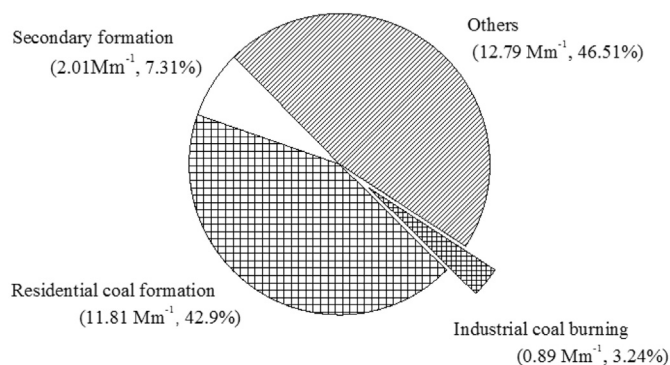


Fig. 5. the source contribution to $b_{\text{abs}365, \text{methanol}}$ using multivariate linear regression model.

Table 2

Relative radiative forcing absorbed by WSOC and MSOC relative to EC in winter over Yulin.

	WSOC/EC	MSOC/EC	WSOC/EC	MSOC/EC
	300–2500 nm		300–400 nm	
Aerosol over Yulin	3.0%	10.8%	11.3%	36.9%
biomass burning		20.3%		83.6%

4.4. Evaluation of radiation forcing by BrC relative to EC

The fractional contribution of solar absorption by light-absorbing WSOC and MSOC relative to that of EC from Yulin was estimated by the following method suggested by Kirillova et al. (2014), as mentioned in the methods section. Table 2 shows the fractional solar absorption of WSOC and MSOC relative to EC. The solar energy directly absorbed by MSOC/EC over the whole solar spectrum was $10.8 \pm 5.6\%$, increasing to $36.9 \pm 13.5\%$ in the UV region (300–400 nm). The absorption figures were lower than those of the biomass-burning source sample ($19.6 \pm 1.0\%$ over the whole solar spectrum and $82.8 \pm 4.3\%$ in the UV region) (Lei et al., 2018). These results highlight that BrC emitted from coal combustion had less influence on radiative forcing than biomass burning.

Finally, the relative radiative forcing by WSOC/EC was also estimated. The solar energy directly absorbed by WSOC/EC ($3.0 \pm 1.0\%$), as expected, was lower than those reported during wintertime in Beijing ($11 \pm 3\%$; Yan et al., 2015) and Delhi ($6 \pm 3\%$; Kirillova et al., 2014). However, the relative radiative forcing of BrC has been underestimated because the solvent extracts that b_{abs} measured were not for PM particles (Liu et al., 2013). Therefore, the contribution of BrC to radiative forcing needs to be reassessed.

5. Conclusions

In this study, optical characteristics and source identification of $\text{PM}_{2.5}$ BrC were conducted over an energy chemical industry city of Yulin in North China. $b_{\text{abs}365, \text{methanol}}$, $\text{AAE}_{\text{methanol}}$ and $\text{MAC}_{365, \text{methanol}}$ of $\text{PM}_{2.5}$ BrC averaged $27.5 \pm 12.0 \text{ Mm}^{-1}$, 5.2 ± 0.8 (330–400 nm), and $1.4 \pm 0.4 \text{ m}^2 \text{ g}^{-1}$, respectively. Comparison of $b_{\text{abs}365}$ between methanol and water extracts suggested that a large portion ($\sim 67.6\%$) of BrC light absorption comes from water insoluble OC. Meanwhile, higher BrC was mainly caused by primary emissions as supported by the strong correlation with POC. The abundance of IP and BaP, as well as high IP/(IP + BghiP) ratio (0.6) revealed that coal burning was the dominant contributor to $\text{PM}_{2.5}$ PAHs. Moreover, a relatively strong positive relationship between $b_{\text{abs}, \text{methanol}}$ and BaP ($r = 0.67$) indicated the important contribution of coal burning to BrC.

Source apportionment based on the PMF model results showed residential coal combustion contributed significantly to the detected

$\text{PM}_{2.5}$ mass (36.9%), followed by industrial coal combustion (21.8%), secondary formation (19.3%), traffic-related emissions (11.7%), and fugitive dust (10.3%). The results from multivariate linear regression highlight that residential coal combustion was the largest contributor to $b_{\text{abs}365, \text{methanol}}$ (37.4%), followed by secondary formation (6.7%) and industrial coal combustion (3.5%). Our study indicates that coal burning is an important contributor to BrC emissions in Yulin. Finally, evaluation of radiation forcing of BrC versus EC showed that the estimated relative radiative forcing by methanol-soluble organic carbon relative to elemental carbon was 36.9% at 300–400 nm over Yulin. These results revealed that BrC emitted from coal combustion had less influence on radiative forcing than biomass burning. It is important to discuss further the seasonal variations of airborne BrC absorption and sources as well as radiative forcing in future work.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (41573101), a grant from SKLLQG, Chinese Academy of Sciences (SKLLQG1616), and the Fundamental Research Funding for Central Universities in China (xkjc2015002).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosres.2018.05.018>.

References

- Alexander, D.T.L., Crozier, P.A., Anderson, J.R., 2008. Brown carbon spheres in east Asian outflow and their optical properties. *Science* 321 (5890), 833–835.
- Arimoto, R., Zhang, X.Y., Huebert, B.J., Kang, C.H., Savoie, D.L., Prospero, J.M., Sage, S.K., Schloesslin, C.A., Khaing, H.M., Oh, S.N., 2004. Chemical composition of atmospheric aerosols from Zhenbeitai, China, and Gosan, South Korea, during ACE-Asia. *J. Geophys. Res. Atmos.* 109 art. no. D19S04.
- Barnard, J.C., Volkamer, R., Kassianov, E.I., 2008. Estimation of the mass absorption cross section of the organic carbon component of aerosols in the Mexico City metropolitan area. *Atmos. Chem. Phys.* 8 (3), 6665–6679.
- Bond, T.C., 2001. Spectral dependence of visible light absorption by carbonaceous particles emitted from coal combustion. *J. Geophys. Res. Lett.* 28 (21), 4075–4078.
- Bond, T.C., Doherty, S.J., Fahey, D.W., Forster, P.M., Bernsten, T., DeAngelo, B.J., Flanner, M.G., Ghan, S., Karcher, B., Koch, D., Kinne, S., Kondo, Y., Quinn, P.K., Sarofim, M.C., Schultz, M.G., Schulz, M., Venkataraman, C., Zhang, H., Zhang, S., Bellouin, N., Guttikunda, S.K., Hopke, P.K., Jacobson, M.Z., Kaiser, J.W., Klimont, Z., Lohmann, U., Schwarz, J.P., Shindell, D., Storelvmo, T., Warren, S.G., Zender, C.S., 2013. Bounding the role of black carbon in the climate system: a scientific assessment. *J. Geophys. Res. Atmos.* 118 (11), 5380–5552.
- Bones, D.L., Henricksen, D.K., Mang, S.A., Gonsior, M., Bateman, A.P., Nguyen, T.B., Cooper, W.J., Nizkorodov, S.A., 2010. Appearance of strong absorbers and fluorophores in limonene- O_3 secondary organic aerosol due to NH_4^+ -mediated chemical aging over long time scales. *J. Geophys. Res.* 115 (D5).
- Cao, J.J., Wu, F., Chow, J.C., Lee, S.C., 2005. Characterization and source apportionment of atmospheric organic and elemental carbon during fall and winter of 2003 in Xi'an, China. *Atmos. Chem. Phys.* 5 (11), 3127–3137.
- Cao, J.J., Shen, Z.X., Chow, J.C., Watson, J.G., Lee, S.C., Tie, X.X., Ho, K.F., Wang, G.H., Han, Y.M., 2012a. Winter and summer $\text{PM}_{2.5}$ chemical compositions in fourteen Chinese cities. *J. Air & Waste Manage. Assoc.* 62 (10), 1214–1226.
- Cao, J.J., Wang, Q.Y., Chow, J.C., Watson, J.G., Tie, X.X., Shen, Z.X., Wang, P., An, Z.S., 2012b. Impacts of aerosol compositions on visibility impairment in Xi'an, China. *Atmos. Environ.* 59, 559–566.
- Chakrabarty, R.K., Moosmüller, H., Chen, L.W.A., Lewis, C.K., 2010. Brown carbon in tar balls from smoldering biomass combustion. *Atmos. Chem. Phys.* 10 (13), 6363–6370.
- Chen, Y., Bond, T.C., 2010. Light absorption by organic carbon from wood combustion. *Atmos. Chem. Phys.* 10, 1773–1787.
- Cheng, Y., He, K.B., Zheng, M., Duan, F.K., 2011. Mass absorption efficiency of elemental carbon and water-soluble organic carbon in Beijing, China. *Atmos. Chem. Phys.* 11 (22), 11497–11510.
- Cheng, T.T., Xu, C., Duan, J.Y., Wang, Y.F., Leng, C.P., Tao, J., Che, H.Z., He, Q.S., Wu, Y.F., Zhang, R.J., Li, X., Chen, J.M., Kong, L.D., Yu, X.N., 2015. Seasonal variation and difference of aerosol optical properties in columnar and surface atmospheres over Shanghai. *Atmos. Environ.* 123, 315–326.
- Cheng, Y., He, K.B., Du, Z.Y., Engling, G., Liu, J.M., Ma, Y.L., Zheng, M., Weber, R.J., 2016. The characteristics of brown carbon aerosol during winter in Beijing. *Atmos. Environ.* 127, 355–364.
- Chow, J.C., Watson, J.G., Chen, L.W.A., Arnott, W.P., Moosmüller, H., 2004. Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols. *Environ. Sci. Technol.* 38, 4414–4422.

- Desyaterik, Y., Sun, Y., Shen, X.H., Lee, T., Wang, X.F., Wang, T., Collett Jr., J.L., 2013. Speciation of "brown" carbon in cloud water impacted by agricultural biomass burning in eastern China. *J. Geophys. Res.* 118 (13), 7389–7399.
- Duan, J., Bi, X., Tan, J., Sheng, G., Fu, J., 2007. Seasonal variation on size distribution and concentration of PAHs in Guangzhou city, China. *Chemosphere* 67 (3), 614.
- Feng, Y., Ramanathan, V., Kotamarthi, V.R., 2013. Brown carbon: a significant atmospheric absorber of solar radiation? *Atmos. Chem. Phys.* 13 (17), 8607–8621.
- Gelencser, A., Hoffer, A., Kiss, G., Tombacz, E., Kurdi, R., Bencze, L., 2003. In-situ formation of light-absorbing organic matter in cloud water. *J. Atmos. Chem.* 45 (1), 25–33.
- Guo, C.F., Wu, Y.S., Chen, J.C., Fu, P.P., Chang, C.N., Ho, T.T., Chen, M.H., 2005. Characteristic study of polycyclic aromatic hydrocarbons for fine and coarse particulates at Pastureland near Industrial Park sampling site of central Taiwan. *Chemosphere* 60 (3), 427–433.
- Guo, R.Y., Shen, Z.X., Ren, W.X., Bie, Z.J., Zhang, Q., Wang, L.Q., Lei, Y.L., 2015. Pollution characteristics of PM₁₀ and PM_{2.5} over Yulin, Shaanxi in winter. *China Powder Science and Technology* 21 (5) (in Chinese).
- Hecobian, A., Zhang, X., Zheng, M., Frank, N., Edgerton, E.S., Weber, R.J., 2010. Water-soluble organic aerosol material and the light-absorption characteristics of aqueous extracts measured over the southeastern United States. *Atmos. Chem. Phys.* 10, 5965–5977.
- Hoffer, A., Gelencser, a., Guyon, P., Kiss, G.G., 2006. Optical properties of humic-like substances (HULIS) in biomass-burning aerosols. *Atmos. Chem. Phys.* 5 (4), 3563–3570.
- Huang, B., Liu, M., Ren, Z.F., Bi, X.H., Zhang, G.H., Sheng, G.Y., Fu, J.M., 2013. Chemical composition, diurnal variation and sources of PM_{2.5} at two industrial sites of South China. *Atmos. Pollut. Res.* 4 (3), 298–305.
- Jacobson, M.Z., 1999. Isolating nitrated and aromatic aerosols and nitrated aromatic gases as sources of ultraviolet light absorption. *J. Geophys. Res.* 104, 3527–3542.
- Jo, D.S., Park, R.J., Lee, S., Kim, S.W., Zhang, X.L., 2015. A global simulation of brown carbon: implications for photochemistry and direct radiative effect. *Atmos. Chem. Phys.* 15 (19), 27805–27852.
- Kirchstetter, T.W., Thatcher, T.L., 2012. Contribution of organic carbon to wood smoke particulate matter absorption of solar radiation. *Atmos. Chem. Phys.* 12, 6067–6072.
- Kirchstetter, T.W., Novakor, T., Hobbs, P.V., 2004. Evidence that the spectral dependence of light absorption by aerosols is affected by organic carbon. *J. Geophys. Res.* 109, D21208. <http://dx.doi.org/10.1029/2004JD004999>.
- Kirilova, E.N., Andersson, A., Tiwari, S., Srivastava, A.K., Bisht, D.S., Gustafsson, O., 2014. Water-soluble organic carbon aerosols during a full New Delhi winter: isotope-based source apportionment and optical properties. *J. Geophys. Res. Atmos.* 119 (6), 3476–3485.
- Lack, D.A., Langridge, J.M., Bahreini, R., Cappa, C.D., Middlebrook, A.M., Schwarz, J.P., 2012. Brown carbon and internal mixing in biomass burning particles. *Proc. Natl. Acad. Sci. U. S. A.* 109 (37), 14802–14807.
- Laskin, J., Laskin, A., Nizkorodov, S.A., Roach, P., Eckert, P., Gilles, M.K., Wang, B., Lee, H.J., Hu, Q., 2014. Molecular selectivity of brown carbon chromophores. *Environ. Sci. Technol.* 48 (20), 12047–12055.
- Laskin, A., Laskin, J., Nizkorodov, S.A., 2015. Chemistry of atmospheric brown carbon. *Chem. Rev.* 115 (10).
- Lei, Y.L., Shen, Z.X., Zhang, T., Zhang, Q., Wang, Q.Y., Sun, J., Gong, X.S., Cao, J.J., Xu, H.M., Liu, S.X., Yang, L., 2018. Optical source profiles of brown carbon in size-resolved particulate matter from typical domestic biofuel burning over Guanzhong Plain, China. *Sci. Total Environ.* 622–623, 244–251.
- Levinson, R., Akbari, H., Berdahl, P., 2010. Measuring solar reflectance- part I: defining a metric that accurately predicts solar heat gain. *Sol. Energy* 84, 1717–1744.
- Lihavainen, H., Alghamdi, M.A., Hyvärinen, A., Hussein, T., Neitola, K., Khoder, M., Abdelmaksoud, A.S., Al-Jeelani, H., Shabbaj, I.I., Almeahmadi, F.M., 2017. Aerosol optical properties at rural background area in Western Saudi Arabia. *Atmos. Res.* 197, 370–378.
- Liu, J., Bergin, M., Guo, H., King, L., Kotra, N., Edgerton, E., Weber, R.J., 2013. Size-resolved measurements of brown carbon in water and methanol extracts and estimates of their contribution to ambient fine-particle light absorption. *Atmos. Chem. Phys.* 13 (24), 12389–12404.
- Liu, Y.R., Zhang, Q.D., Wang, W., Liu, Z.L., Zhu, X.Y., Tian, S.B., 2014. Changes of petroleum acid distribution characterized by FT-ICR MS in heavy acidic crude oil after true boiling point distillation. *China Petroleum Processing & Petrochemical Technology* 16 (1), 8–12.
- Lukacs, H., Gelencser, A., Hammer, S., Puxbaum, H., Pio, C., Legrand, M., Giebl, A.K., Handler, M., Limbeck, A., Simpson, D., 2007. Seasonal trends and possible sources of brown carbon based on 2-year aerosol measurements at six sites in Europe. *J. Geophys. Res.* 112 (D23), 4789–4797.
- Mohr, C., Lopezhilfiker, F.D., Zotter, P., Prevot, A.S., Xu, L., Ng, N.L., Herndon, S.B., Williams, L.R., Franklin, J.P., Zahniser, M.S., Worsnop, D.R., Knighton, W.B., Aiken, A.C., Gorkowski, K.J., Duebey, K.K., Allan, J.D., Thornton, J.A., 2013. Contribution of nitrated phenols to wood burning brown carbon light absorption in Detling, United Kingdom during winter time. *Environ. Sci. Technol.* 47 (12), 6316–6324.
- Paatero, P., Tapper, U., 1994. Positive matrix factorization: a non-negative factor model with optimal utilization of error estimates of data values. *Environmetrics* 5 (2), 111–126.
- Park, S.S., Son, S.C., 2017. Relationship between carbonaceous components and aerosol light absorption during winter at an urban site of Gwangju, Korea. *Atmos. Res.* 185, 73–83.
- Park, S.S., Yu, G.H., Lee, S., 2018. Optical absorption characteristics of brown carbon aerosols during the KORUS-AQ campaign at an urban site. *Atmos. Res.* 203, 16–27.
- Ram, K., Sarin, M.M., 2011. Day-night variability of EC, OC, WSOC and inorganic ions in urban environment of indo-Gangetic plain: implications to secondary aerosol formation. *Atmos. Environ.* 45 (2), 460–468.
- Sawicki, E., 1962. Analysis for airborne particulate hydrons, their relative proportion affected by different types of pollution. *Nat. Cancer Inst. Monograph* 9 (6), 201–208.
- Shakeri, A., Madadi, M., Mehrabi, B., 2016. Health risk assessment and source apportionment of PAHs in industrial and bitumen contaminated soils of Kermanshah province; NW Iran. *Toxicol. & Environ. Health. Sci.* 8 (3), 201–212.
- Shen, Z.X., Arimoto, R., Cao, J.J., Zhang, R.J., Li, X.X., Du, N., Okuda, T., Nakao, S., Tanaka, S., 2008. Seasonal variations and evidence for the effectiveness of pollution controls on water-soluble inorganic species in total suspended particulates and fine particulate matter from Xi'an, China. *J. Air Waste Manag. Assoc.* 58, 1560–1570.
- Shen, Z.X., Cao, J.J., Arimoto, R., Han, Z.W., Zhang, R.J., Han, Y.M., Liu, S.X., Okuda, T., Nakao, S., Tanaka, S., 2009. Ionic composition of TSP and PM_{2.5} during dust storms and air pollution episodes at Xi'an, China. *Atmos. Environ.* 43, 2911–2918.
- Shen, Z.X., Cao, J.J., Arimoto, R., Han, Y.M., Zhu, C.S., Tian, J., Liu, S.X., 2010. Chemical characteristics of fine particle (PM₁) from Xi'an, China. *Aerosol Sci. Technol.* 44 (6), 461–472.
- Shen, Z.X., Zhang, Q., Cao, J.J., Zhang, L.M., Lei, Y.L., Huang, Y., Huang, R.J., Gao, J.J., Zhao, Z.Z., Zhu, C.S., Yin, X.L., Zheng, C.L., Xu, H.M., Liu, S.X., 2017a. Optical properties and possible sources of brown carbon in PM_{2.5} over Xi'an, China. *Atmos. Environ.* 150, 322–330.
- Shen, Z.X., Lei, Y.L., Zhang, L.M., Zhang, Q., Zeng, Y.L., Tao, J., Zhu, C.S., Cao, J.J., Xu, H.M., Liu, S.X., 2017b. Methanol extracted Brown Carbon in PM_{2.5} over Xi'an, China: seasonal variation of optical properties and sources identification. *Aerosol. Sci. Engineering* 1–9.
- Srinivas, B., Sarin, M.M., 2014. Brown carbon in atmospheric outflow from the Indo-Gangetic Plain: mass absorption efficiency and temporal variability. *J. Atmos. Environ.* 89, 835–843.
- Sun, Y.L., Wang, Z.F., Fu, P.Q., Yang, T., 2013. Aerosol composition, sources and processes during wintertime in Beijing, China. *Atmos. Chem. Phys.* 13 (9), 4577–4592.
- Tao, J., Zhang, L.M., Cao, J.J., Hsu, S.C., Xia, X.G., Zhang, Z.S., Lin, Z.J., Cheng, T.T., Zhang, R.J., 2014. Characterization and source apportionment of aerosol light extinction and source apportionment of aerosol light extinction in Chengdu, southwest China. *Atmos. Environ.* 95 (1), 552–562.
- Tao, J., Zhang, L.M., Cao, J.J., Zhang, R.J., 2017. A review of current knowledge concerning PM_{2.5} chemical composition, aerosol optical properties, and their relationships across China. *Atmos. Chem. Phys.* 1–70.
- Teich, M., Pinxteren, D.V., Wang, M., Kecorius, S., Wang, Z.B., Müller, T., Mocnik, G., Herrmann, H., 2017. Contributions of nitrated aromatic compounds to the light absorption of water-soluble and particulate brown carbon in different atmospheric environments in Germany and China. *Atmos. Chem. Phys.* 1–24.
- Turpin, B.J., Lim, H.J., 2001. Species contributions to PM_{2.5} mass concentrations: revisiting common assumptions for estimating organic mass. *Aerosol Sci. Technol.* 35 (1), 602–610.
- Wan, X., Kang, S.C., Xin, J.Y., Liu, B., Wen, T.X., Wang, P.L., Wang, Y.S., Cong, Z.Y., 2016. Chemical composition of size-segregated aerosols in Lhasa city, Tibetan Plateau. *Atmos. Res.* 174–175, 142–150.
- Wang, Q.Y., Huang, R.J., Zhao, Z.Z., Zhang, N.N., Wang, Y.C., Ni, H.Y., Tie, X.X., Han, Y.M., Zhuang, M.Z., Wang, M., Zhang, J.R., Zhang, X.M., Dusek, U., Cao, J.J., 2016a. Size distribution and mixing state of refractory black carbon aerosol from a coastal city in South China. *Atmos. Res.* 181, 163–171.
- Wang, Q.Y., Huang, R.J., Zhao, Z.Z., Cao, J.J., Ni, H.Y., Tie, X.X., Zhao, S.Y., Su, X.L., Han, Y.M., Shen, Z.X., Wang, Y.C., Zhang, N.N., Zhou, Y.Q., Corbin, J.C., 2016b. Physicochemical characteristics of black carbon aerosol and its radiative impact in a polluted urban area of China. *J. Geophys. Res. Atmos.* 121 (20), 12505–12519.
- Watson, J.G., Chow, J.C., Houck, J.E., 2001. PM_{2.5} chemical source profiles for vehicle exhaust, vegetative burning, geological material, and coal burning in northwestern Colorado during 1995. *Chemosphere* 43, 1141–1151.
- Xiao, S., Wang, Q.Y., Cao, J.J., Huang, R.J., Chen, W.D., Han, Y.M., Xu, H.M., Liu, S.X., Zhou, Y.Q., Wang, P., Zhang, J.Q., Zhan, C.L., 2014. Long-term trends in visibility and impacts of aerosol composition on visibility impairment in Baoji, China. *Atmos. Res.* 149, 88–95.
- Yan, C.Q., Zheng, M., Sullivan, A.P., Bosch, C., Desyaterik, Y., Andersson, A., Li, X.Y., Guo, X.S., Zhou, T., Gustafsson, O., Collett Jr., J.L., 2015. Chemical characteristics and light-absorbing property of water-soluble organic carbon in Beijing: biomass burning contributions. *Atmos. Environ.* 121, 4–12.
- Yang, M., Howell, S.G., Zhuang, J., Huebert, B.J., 2009. Attribution of aerosol light absorption to black carbon, brown carbon, and dust in China: interpretations of atmospheric measurements during EAST-AIRE. *Atmos. Chem. Phys.* 8 (3), 10913–10954.
- Yuan, J.F., Huang, X.F., Cao, J.M., Cui, J., Zhu, Q., Huang, C.N., Lan, Z.J., He, L.Y., 2016. Light absorption of brown carbon aerosol in the PRD region of China. *Atmos. Chem. Phys.* 15 (20), 28453–28482.
- Zhang, X.L., Lin, Y.H., Surratt, J.D., Zotter, P., Prevot, A.S.H., Weber, R.J., 2011. Light-absorbing soluble organic aerosol in Los Angeles and Atlanta: a contrast in secondary organic aerosol. *Geophys. Res. Lett.* 38 (21), 759–775.
- Zhang, X.L., Lin, Y.H., Surratt, J.D., Weber, R.J., 2013. Sources, composition and absorption Ångström exponent of light-absorbing organic components in aerosol extracts from the Los Angeles Basin. *Environ. Sci. Technol.* 47, 3685–3693.
- Zhang, Q., Shen, Z.X., Cao, J.J., Ho, K.F., Zhang, R.J., Bie, Z.J., Chang, H.R., Liu, S.X., 2014. Chemical profiles of urban fugitive dust over Xi'an in the south margin of the loess plateau, China. *Atmos. Pollut. Res.* 5 (3), 421–430.
- Zhou, Y.Q., Wang, Q.Y., Huang, R.J., Liu, S.X., Tie, X.X., Su, X.L., Niu, X.Y., Zhao, Z.Z., Ni, H.Y., Wang, M., Zhang, Y.G., Cao, J.J., 2017. Optical properties of aerosols and implications for radiative effects in Beijing during the Asia-Pacific economic cooperation summit 2014. *J. Geophys. Res. Atmos.* 122 (18).