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Characterization of carbonaceous fractions in PM$_{2.5}$ and PM$_{10}$ over a typical industrial city in central China

Changlin Zhan[1] · Jiaquan Zhang[1] · Jingru Zheng[1] · Ruizhen Yao[1] · Ping Wang[2] ·
Hongxia Liu[1] · Wensheng Xiao[1] · Xianli Liu[1] · Junji Cao[3,4]

Abstract Aerosol samples of PM$_{2.5}$ and PM$_{10}$ were collected every 6 days from March 2012 to February 2013 in Huangshi, a typical industrial city in central China, to investigate the characteristics, relationships, and sources of carbonaceous species. The PM$_{2.5}$ and PM$_{10}$ samples were analyzed for organic carbon (OC), elemental carbon (EC), char, and soot using the thermal/optical reflectance (TOR) method following the IMPROVE_A protocol. PM$_{2.5}$ and PM$_{10}$ concentrations ranged from 29.37 to 501.43 µg m^{-3} and from 50.42 to 330.07 µg m^{-3}, with average levels of 104.90 and 151.23 µg m^{-3}, respectively. The 24-h average level of PM$_{2.5}$ was about three times the US EPA standard of 35 µg m^{-3}, and significantly exceeds the Class II National Air Quality Standard of China of 75 µg m^{-3}. The seasonal cycles of PM mass and OC concentrations were higher during winter than in summer. EC and char concentrations were generally highest during winter but lowest in spring, while higher soot concentrations occurred in summer. This seasonal variation could be attributed to different seasonal meteorological conditions and changes in source contributions. Strong correlations between OC and EC were found for both PM$_{2.5}$ and PM$_{10}$ in winter and fall, while char and soot showed a moderate correlation in summer and winter. The average OC/EC ratios were 5.11 and 4.46 for PM$_{2.5}$ and PM$_{10}$, respectively, with individual OC/EC ratios nearly always exceeding 2.0. Higher char/soot ratios during the four seasons indicated that coal combustion and biomass burning were the major sources for carbonaceous aerosol in Huangshi. Contrary to expectations, secondary organic carbon (SOC) which is estimated using the EC tracer method exhibited spring maximum and summer minimum, suggesting that photochemical activity is not a leading factor in the formation of secondary organic aerosols in the study area. The contribution of SOC to OC concentration for PM$_{2.5}$ and PM$_{10}$ were 47.33 and 45.38%, respectively, implying that SOC was an important component of OC mass. The serious air pollution in haze-fog episode was strongly correlated with the emissions of pollutants from biomass burning and the meteorological conditions.

Keywords PM$_{2.5}$ · PM$_{10}$ · Organic carbon (OC) · Elemental carbon (EC) · Source

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✉ Changlin Zhan
zhancl@ieecas.cn; chl_zhan@126.com

[1] Environmental Science and Engineering Collage, Hubei Polytechnic University, Huangshi 435003, China

[2] School of Tropical Eco-environment Protection, Hainan Tropical Ocean University, Sanya 572022, China

[3] Key Laboratory of Aerosol Chemistry and Physics (KLACP), Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710061, China

[4] Institute of Global Environmental Change, Xi'an Jiaotong University, Xi'an 710049, China

Introduction

In the last few decades, various studies have been carried out on atmospheric aerosol due to its adverse effects on air quality and visibility (Bäumer et al. 2008; Cao et al. 2012a), regional and global climates (Booth et al. 2012; Kaufman et al. 2002; Lohmann and Feichter 2005; Paasonen et al. 2013; Ramanathan et al. 2001), and human health (Cao et al. 2012b; Kan et al. 2004; Pope et al. 2002). Particles, containing PM$_{10}$ and PM$_{2.5}$ (particulate matter with an aerodynamic diameter less than 10 and 2.5 µm, respectively), are an important component of atmospheric

carbonaceous aerosols. The carbonaceous aerosols are mainly composed of organic carbon (OC) and elemental carbon (EC). OC is directly derived from primary sources (fossil fuel combustion and biomass burning) or produced from atmospheric chemical reactions between volatile organic reactive species and gas-phase precursors. EC is a constituent of combustion residues and combustion emissions, ranging from large pieces of slightly charred material (1–100 mm) to highly condensed refractory submicron soot particles (30–40 nm) (Masiello 2004), mainly from primary anthropogenic sources (vehicular exhausts and combustion of fossil fuel/biomass burning), and can be subdivided into two classes: char and soot (Han et al. 2007, 2010). Char and soot have different chemical and optical properties; thus, their effects on climate and environment may be differed from each other. Thus, differentiation and measurement of char and soot would help us better understand the possible emission sources and their climatic impacts, and provide useful information about air pollution control.

The pollution of particulate matter (PM) has become a serious environmental problem in many regions of the world, especially in South Asia. It is estimated that China contributes roughly one fifth of the global carbonaceous emissions (Bond et al. 2004). In recent years, elevated pollution with PM concentration as high as several hundreds of micrograms per cubic meter has been reported in many mega-cities in China, such as Beijing, Xi'an, Shanghai, Guangzhou, and Chengdu. Furthermore, many regions of China even experienced extremely severe and continuous haze-fog pollution each year (Huang et al. 2014; Sun et al. 2006; Wang et al. 2014; Zheng et al. 2015), which induce potential harmful impact on human health. Thus, carbonaceous aerosol in China has received increasing and special attentions. There are many studies focusing on the field measurements of carbonaceous abundance in PM in China's industrialized areas, such as Beijing, Xi'an, Guangzhou, Hong Kong, Shanghai, Nanjing, and other cities. These study areas are mainly concentrated in the regions of Beijing-Tianjin-Hebei (BTH), Pearl River Delta (PRD), and Yangtze River Delta (YRD). However, there is little continuous study conducted in central China (Lyu et al. 2016; Xiong et al. 2017).

Huangshi, an industrial city with long-lasting history of mining and smelting, is located in the middle and lower reaches of the Yangtze River in China. Since the Ying and Shang Dynasty, mining and metallurgy in Huangshi is in prosperity. Thus, there is a long-run relationship between economic growth and mining and metallurgy in this city. Coal-based metal smeltering caused large amounts of pollutants (e.g., particles, metals, PAHs, and black carbon) emitted in this region. Previous studies showed that the contribution of coal combustion to total carbon in $PM_{2.5}$ in Xi'an reached 44% (Cao et al. 2005), and a relatively high contribution from coal burning to $PM_{2.5}$ (9~21%) in Beijing and Xi'an has also been found (Huang et al. 2014).

The present work is focused on the characteristics of carbonaceous components of $PM_{2.5}$ and PM_{10} in Huangshi City. The objectives of this study are to (1) determine the pollution levels and seasonal characteristics of carbonaceous species in $PM_{2.5}$ and PM_{10}, (2) investigate the relationship between OC vs. EC and char vs. soot in $PM_{2.5}$ and PM_{10}, (3) estimate SOC production during the sampling period, and (4) identify the emission source of OC and EC in $PM_{2.5}$ and PM_{10} through principal component analysis (PCA).

Experimental

Sampling location and sample collection

Huangshi City, located in southeast of Hubei province, is also an important industrial base for raw materials in central China. As such, the city has profound industrial culture, which is known as "the Hometown of Bronze" and "the Cradle of Steel." It has a typical subtropical continental monsoon climate, with mean annual temperature of 17 °C and mean precipitation of 1382.6 mm. There were no major industrial activities surrounding the sampling location.

The sampling site (30° 12′ 35.71″ E, 115° 01′ 30.75″ N) is on the roof of a fifth-floor building (about 12 m high) of Hebei Polytechnic University campus (Fig. 1). The $PM_{2.5}$ and PM_{10} daily samples were collected once every 6 days from March 2012 to February 2013. Sampling was conducted using two battery-powered mini-volume samplers (Airmetrics, Oregon, USA) with a flow rate of 5 L min^{-1} and started at 09:00 a.m. any day to 09:00 a.m. the next day. Twenty-four-hour $PM_{2.5}$ and PM_{10} samples were collected on 47-mm Whatman quartz microfiber filters (preheated at 800 °C for 3 h to remove any absorbed organic materials). Field blank filters were also collected to subtract the positive artifacts due to the absorption of gasphase organic components onto the filter during and/or after sampling. All the samples were wrapped in baked aluminum foil and placed in zip lock bags, and then stored under airtight conditions in a refrigerator at approximately 4 °C before chemical analysis to prevent evaporation of volatilized components. Meteorological data (wind speed, wind direction, temperature, and relative humidity) during the sampling period were obtained from Weather Underground (http://www.wunderground.com/).

Mass analysis

The aerosol mass concentrations were determined gravimetrically using an electronic microbalance with 1 μg sensitivity (Sartorius, Göttingen, Germany) at the Institute of Earth Environment, Chinese Academy of Sciences. Before weighting, the filters were equilibrated for 24 h at constant

Fig. 1 Location of the sampling site at Huangshi, China
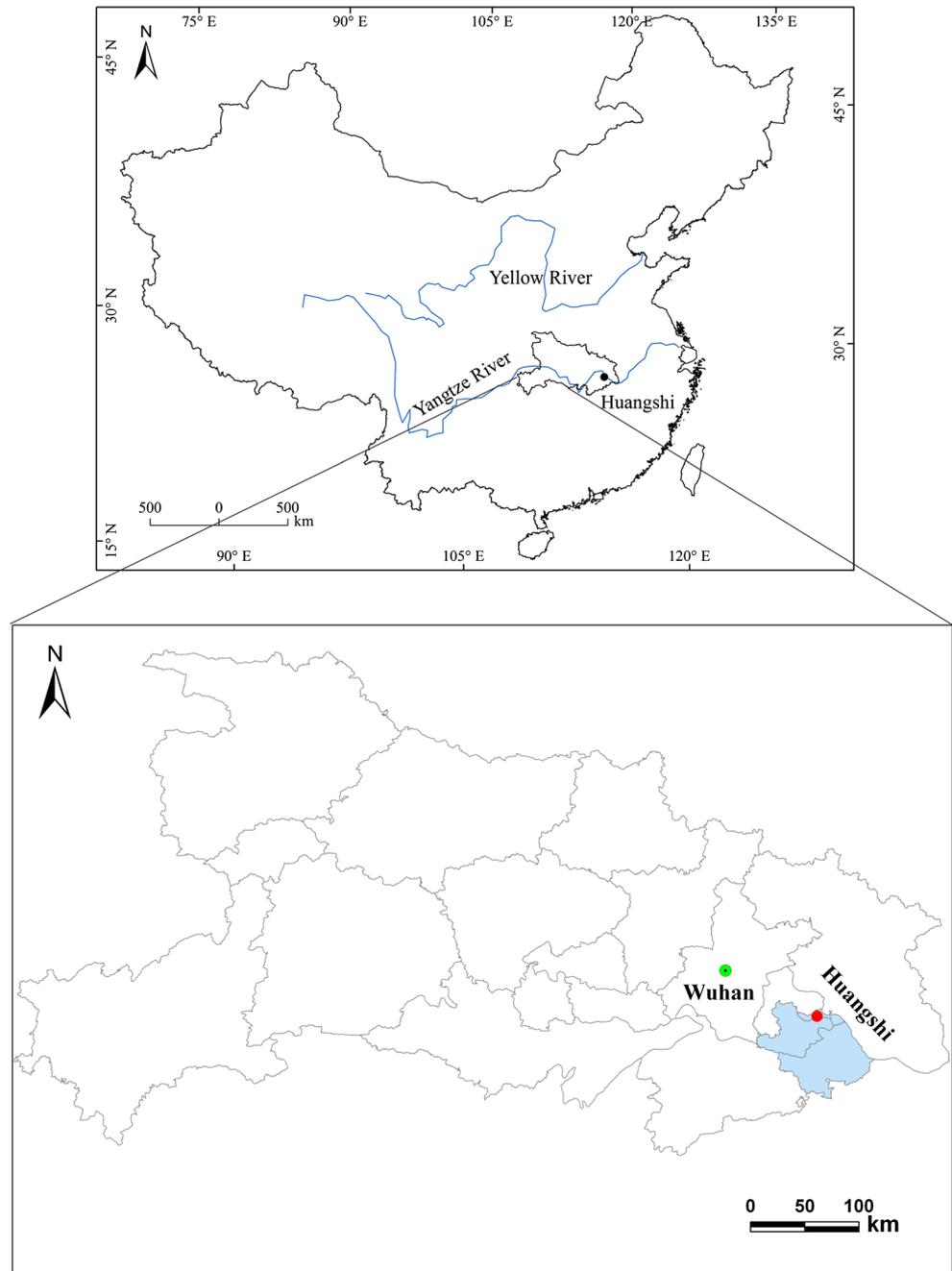
temperature (20–23 °C) and relative humidity (35–45%). Each filter was weighed at least three times before and after the sampling by a 24-h equilibration. The mean net mass for each filter was obtained by averaging the mass differences between the pre- and the post-weighting data. The precision of the weighing process was < 10 μg for the blank filters and < 20 μg for the filter samples. Therefore, the precision of weight measurements should be 20 μg for filter samples.

Carbon analysis

Carbon analysis were carried out using a DRI Model 2001 carbon analyzer (Atmoslytic Inc., Calabasas, CA, USA), which employs thermal/optical reflectance (TOR) following the IMPROVE_A protocol (Cao et al. 2013; Chow et al. 2007). A 0.526-cm^2 punch from each quartz filter sample was placed at the sample load position of the analyzer and heated in a stepwise manner. This produced four OC fractions

(OC1, OC2, OC3, and OC4 in a helium atmosphere at 140°, 280°, 480°, and 580 °C, respectively), a pyrolyzed carbon fraction (OP, determined when reflected laser light attained its original intensity after oxygen was added to the combustion atmosphere), and three EC fractions (EC1, EC2, and EC3 in a mixture of 2% O_2 and 98% helium carrier gas at 580°, 740°, and 840 °C, respectively). Total OC is operationally defined as OC1 + OC2 + OC3 + OC4 + OP, and total EC is defined as EC1 + EC2 + EC3 − OP. The EC fraction was further divided into char and soot according to Han et al. (2007, 2009), who defined char as EC1 − OP and soot as EC2 + EC3, respectively. The detection limits for EC and OC are below 0.1 μg cm^{-2}.

Results and discussion

Mass, OC, EC, char, and soot in $PM_{2.5}$ and PM_{10}

Descriptive statistics of measurement results for 24-h average concentrations of $PM_{2.5}$ and PM_{10} mass, total carbon (TC), OC, EC, char, and soot during the sampling period are presented in Table 1. The levels of $PM_{2.5}$ and PM_{10} mass in the observation period varied between 29.4–501.4 and 50.4–330.1 μg m^{-3}, with averaged values of 104.9 and 151.2 μg m^{-3}, respectively. These values have exceeded the Second Annual Ambient Air Quality Standard of $PM_{2.5}$ (75 μg m^{-3}) and PM_{10} (150 μg m^{-3}) by the China Environmental Protection Administration. The highest concentration of $PM_{2.5}$ even reached up to 501.4 μg m^{-3} on 11 June 2012, reflecting higher emissions and serious pollution. This extremely high $PM_{2.5}$ concentration presented a great risk to human health. Generally, the mean $PM_{2.5}$ concentration observed at this study (104.9 μg m^{-3}) was higher than those previously found in Hong Kong, Shenzhen, and Zhuhai in winter of 2002 (Cao et al. 2003), but lower than the levels measured in northern Chinese cities, such as Beijing, Xi'an, and Changchun in summer and winter of 2003 (Cao et al. 2007). The significant spatial variation was probably related

to the differences on emission sources and atmospheric conditions.

The $PM_{2.5}$ OC and EC concentrations were 4.9–127.6 and 0.5–15.6 μg m^{-3}, with mean values of 17.9 and 5.2 μg m^{-3} (Table 1), contributing to 81.4 and 83.9% of those in PM_{10}, respectively, indicating that OC and EC are concentrated in the fine particles and greater importance of anthropogenic sources. The average OC and EC concentrations in $PM_{2.5}$ are higher than those measured in Shenzhen (9.6 μg m^{-3} for OC and 4.7 μg m^{-3} for EC during January–February 2001; Cao et al. 2003), Shanghai (6.8 μg m^{-3} for OC and 1.8 μg m^{-3} for EC in September 2009; Cao et al. 2013), Saitama (5.5 μg m^{-3} for OC and 3.1 μg m^{-3} for EC during July 2009–April 2010; Kim et al. 2011a), and Madrid (3.8 μg m^{-3} for OC and 3.8 μg m^{-3} for EC during June 2009 –February 2010; Pio et al. 2011), but significantly lower than those in Xi'an (34.1 μg m^{-3} for OC and 11.3 μg m^{-3} for EC during September 2003–February 2004; Cao et al. 2005) and Chongqing (50.9 μg m^{-3} for OC and 12.3 μg m^{-3} for EC in 2003; Cao et al. 2007) (Table 2). This is probably due to relatively unfavorable meteorological conditions and the great contribution of coal combustion emissions in these urban sites. The greater variability for OC in $PM_{2.5}$ is presumably due to the complexity of emission sources, most especially those resulting in the formation of secondary organic carbon (SOC). In comparison, OC and EC in PM_{10} ranged between 7.8 and 46.6 and between 1.4 and 14.3 μg m^{-3}, with averaged values of 22.0 and 6.2 μg m^{-3}, respectively. These OC and EC concentrations are significantly higher than those measured at Gosan (4.7 μg m^{-3} for OC and 1.7 μg m^{-3} for EC during August 2007–September 2008; Lim et al. 2012), but lower than those measured in Xi'an (43.2 μg m^{-3} for OC and 15.0 μg m^{-3} for EC during September 2003–February 2004 μg m^{-3}; Cao et al. 2005) (Table 2). On average, carbonaceous matter (CM), which is the sum of organic matter (OM = 1.6 × OC) (Turpin and Lim 2001) and EC, constituted 35.67% of $PM_{2.5}$ vs. 26.49% in PM_{10}. Although our result was a little lower than the average fraction of CM in $PM_{2.5}$ found in 14 Chinese cities in summer

Table 1 Demographic data of patients with ALS, CVD, and healthy control

Analyte	$PM_{2.5}$		PM_{10}	
	Range	Average[a]	Range	Average[a]
Mass	29.4–501.4	104.9	50.4–330.1	151.2
OC	4.9–127.6	17.9	7.8–46.6	22.0
EC	0.5–15.6	5.2	1.4–14.3	6.2
Char	0.3–14.3	4.5	0.9–13.0	5.3
Soot	0.1–2.3	0.7	0.3–2.5	0.9
OC/EC	1.8–23.9	5.2	1.9–13.7	4.5
Char/soot	1.3–26.9	8.0	0.9–19.3	6.6

[a] All concentrations are given as mean ± standard deviation in micrograms per cubic meter

Table 2 Comparison of OC and EC concentrations, and OC/EC ratios in $PM_{2.5}$ and PM_{10} between different cities

City	Period	Sample category	OC (μg m^{-3})	EC (μg m^{-3})	OC/EC	Measure method	Reference
Huangshi, China	March 2012–February 2013	$PM_{2.5}$	17.85	5.15	5.2	Thermal optical	This study
Beijing, China	Winter of 2002	$PM_{2.5}$	36.7	15.2	3.5	Thermal optical	Dan et al. (2004)
Xi'an, China	Fall of 2003	$PM_{2.5}$	34.1	11.3	3.3	Thermal optical	Cao et al. (2005)
Shanghai, China	September 2009	$PM_{2.5}$	6.79	1.76	3.9	Thermal optical	Cao et al. (2013)
Shenzhen, China	Winter of 2001	$PM_{2.5}$	13.2	6.1	2.2	Thermal optical	Cao et al. (2003)
Gosan, Korea	August 2007–September 2008	$PM_{2.5}$	4.0	1.7	2.3	Thermal optical	Lim et al. (2012)
Saitama, Japan	July 2009–April 2010	$PM_{2.5}$	5.5	3.1	1.91	Thermal optical	Kim et al. (2011a)
Madrid, Spain	June 2009–February 2010	$PM_{2.5}$	3.8	3.8	1.0	Thermal optical	Turpin and Huntzicker (1995)
Huangshi, China	March 2012–February 2013	PM_{10}	20.03	6.20	4.5	Thermal optical	This study
Xi'an, China	Fall of 2003	PM_{10}	43.2	15.0	3.2	Thermal optical	Cao et al. (2005)
Guangzhou, China	Winter of 2001	PM_{10}	29.4	10.4	2.7	Thermal optical	Cao et al. (2003)
Hong Kong, China	Winter of 2001	PM_{10}	10.5	5.1	2.3	Thermal optical	Cao et al. (2003)
Gosan, Korea	August 2007–September 2008	PM_{10}	4.7	1.7	2.8	Thermal optical	Lim et al. (2012)
Birmingham, UK	May 2004–April 2005	PM_{10}	4.3	1.2	4.0	Thermal optical	Pio et al. (2011)

(38.8%) and winter (44.2%) of 2003 (Cao et al. 2007), it indicates that carbon is still an important $PM_{2.5}$ component in Huangshi City.

Both char and soot were predominant in the $PM_{2.5}$ and PM_{10} fractions: char averaged 4.5 μg m^{-3} in $PM_{2.5}$ vs. 5.3 μg m^{-3} in PM_{10}, while the corresponding values for soot were 0.7 μg m^{-3} in $PM_{2.5}$ vs. 0.9 μg m^{-3} in PM_{10} (Table 1). The average char and soot concentrations in $PM_{2.5}$ accounted for 87.3 and 12.7% of the total EC, respectively, indicating that the contribution of char was significant in Huangshi. The char and soot levels in $PM_{2.5}$ seem lower than those reported in Xi'an (Han et al. 2010), but higher than those found in Saitama, a city in Japan (Kim et al. 2011b). This discrepancy

can be attributed to the difference in the amounts of coal consumption. Interestingly, our soot values was comparable to those measured in Shanghai (Cao et al. 2013) and a small village in Daihai, Inner Mongolia, China (Han et al. 2008), which may be related to the submicron particle size of soot that facilitates it to be regionally and globally dispersed.

Seasonal patterns of PM mass, OC, EC, char, and soot

The $PM_{2.5}$ and PM_{10} mass exhibited clear seasonal variations. Seasonal mass fractions of major carbonaceous components (OC, EC, char, and soot) and mass concentrations are compared in Fig. 2. The average 24-h $PM_{2.5}$ mass were higher in

Fig. 2 Seasonal variations of mass concentrations and OC, EC, char, and soot against mass in $PM_{2.5}$ and PM_{10}
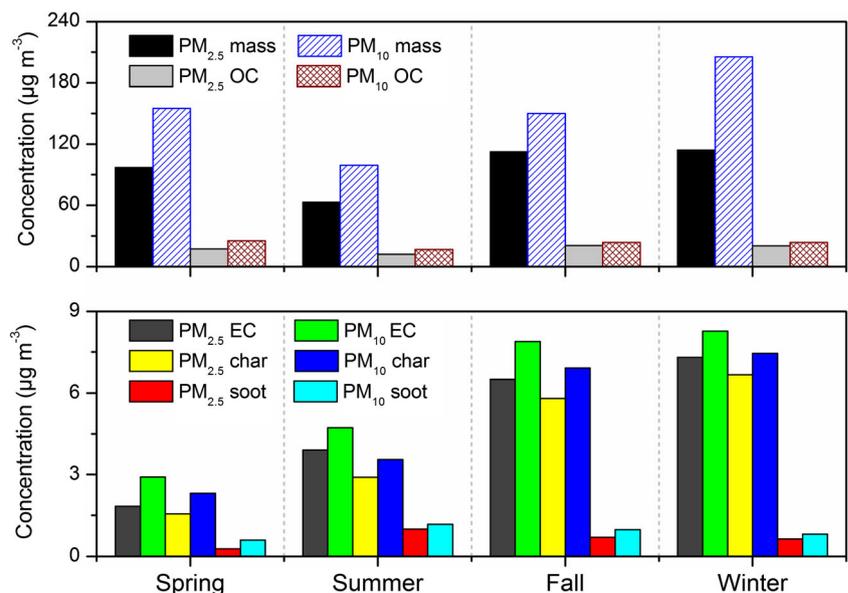
winter (114.0 μg m^{-3}) and lower in summer (62.0 μg m^{-3}, except for the haze-fog episode on 11 June 2012). The PM$_{2.5}$ level in winter was a little higher than the annual average value, while the averaged PM$_{10}$ level was also found higher in winter (205.5 μg m^{-3}) and lower in summer (99.1 μg m^{-3}). This seasonal pattern is consistent with many previous studies in other urban sites of the world (Gu et al. 2010; Lim et al. 2012). Generally, the PM concentrations in winter were higher than those of summer by a factor of 1.8 for PM$_{2.5}$ and 2.1 for PM$_{10}$, indicating a stronger seasonal impact on coarse particles. The higher mass concentration found in winter could be related to the lower ambient temperature and lower mixing layer height in winter, thus preventing the diffusion of atmospheric pollutants. Moreover, it may not neglect the emission sources from far-away regions by long-range transport. Under the influence of the East Asian monsoon circulation, precipitation frequently happens during summer in Huangshi City, which promotes the scavenging of aerosol particles and greatly relieves ambient air pollution to some degree.

Highlighted in Fig. 2, OC and EC concentrations in PM$_{2.5}$ and PM$_{10}$ showed similar seasonal variations as PM masses. The PM$_{2.5}$ OC exhibited higher concentrations in fall and winter and lower concentrations in spring and summer, and ranked in the order of winter > fall > spring > summer. This pattern is consistent with other studies carried out in various sites in China and Europe (Gu et al. 2010; Paraskevopoulou et al. 2014; Schwarz et al. 2008; Yang et al. 2005a; Zhao et al. 2013). The higher OC concentrations during cold winter time are likely related to secondary formation by condensation processes. The PM$_{2.5}$ OC levels in winter were higher than in summer by nearly two times, while the PM$_{10}$ OC concentrations were in the order of spring > winter > fall > summer and the values in winter and fall were almost equivalent. EC fractions for PM$_{2.5}$ and PM$_{10}$ were more predominant in winter. This is because EC is a primary product derived from combustion emissions, primarily coal combustion and vehicle exhaust. The higher concentrations in winter are possibly due to the unfavorable meteorological conditions which is not suitable for the dispersion processes. Different from OC fraction, the minimum EC values for PM$_{2.5}$ and PM$_{10}$ occurred in spring.

Char and soot concentrations showed different seasonal variations. Char concentrations of PM$_{2.5}$ and PM$_{10}$ were in the order of winter > fall > summer > spring, while soot was in the order of summer > fall > winter > spring (Fig. 2). The higher char concentrations during winter reflected that increasing emissions from coal combustion and biomass burning related to resident heating. In contrast, the highest soot concentrations in summer were likely due to long-distance transport by summer monsoon from the adjacent cities because farmland straw burning is very prevalent in central China. Han et al. (2010) collected PM$_{2.5}$ particles in Xi'an,

the result of which was different from our observation that both char and soot had minimum levels in summer. Lim et al. (2012) conducted a study on PM$_{1.0}$ and PM$_{10}$ particles in Gosan, Japan, and showed that a minimum concentration of char was found in summer but soot was relatively higher during summer. This difference could be attributed to the combined effect of different meteorologies in each season and changes in emission sources and rates.

Relationships between OC vs. EC and char vs. soot

The relationship between OC and EC is very useful in assessing the origin of carbonaceous aerosols (Cao et al. 2005; Chow et al. 1996; Turpin and Huntzicker 1995). As shown in Fig. 3a, OC had strong correlation with EC for PM$_{2.5}$ in winter ($r = 0.91$), spring ($r = 0.78$), and fall ($r = 0.76$), which suggests common dominant emission sources such as biomass burning, motor vehicular exhaust, and/or coal combustion for OC and EC. However, the correlation between OC and EC was very poor in summer for PM$_{2.5}$ ($r = 0.30$), implying that OC and EC derived from different sources during this period. OC and EC were highly correlated in PM$_{10}$ for winter ($r = 0.92$) and fall ($r = 0.78$), but not distinctly correlated in spring ($r = 0.39$) and summer ($r = 0.12$, Fig. 3b). Generally, EC is emitted from primary anthropogenic sources, whereas OC may be directly emitted or formed by photochemical reactions leading to production of secondary organic aerosols. The relationship between OC and EC in this study is different from those observed in Beijing (Yang et al. 2005a), Shanghai (Feng et al. 2009), and Tianjin (Gu et al. 2010), the results of which indicate that stronger correlations of OC and EC were found for the four seasons. This discrepancy may be attributed to seasonal variability and intercity difference in OC contributions from emission sources.

Char was poorly correlated with soot for PM$_{2.5}$ in spring ($r = 0.20$) and fall ($r = 0.12$), but higher correlations were found in winter ($r = 0.77$) and summer ($r = 0.64$, Fig. 3c). Similarly, the correlations between char and soot were higher for PM$_{10}$ in summer ($r = 0.46$) and winter ($r = 0.52$), but poor correlations were found in spring ($r = -0.1$) and fall ($r = 0.27$, Fig. 3d). This finding is different from the previous study in Xi'an (Han et al. 2010). For example, Han et al. (2010) found that char was moderately correlated with soot in PM$_{2.5}$ for spring and summer, while the study in 14 Chinese cities conducted by Han et al. (2009) showed very poor correlations between char and soot both in winter and summer. Another study reported a moderate negative correlation between char with soot in PM$_{2.5}$ in Saitama city, Japan (Kim et al. 2011b). It partly can be explained by the different formation mechanisms of char and soot. One other reason can be related to the different emission sources of char and soot in different seasons.
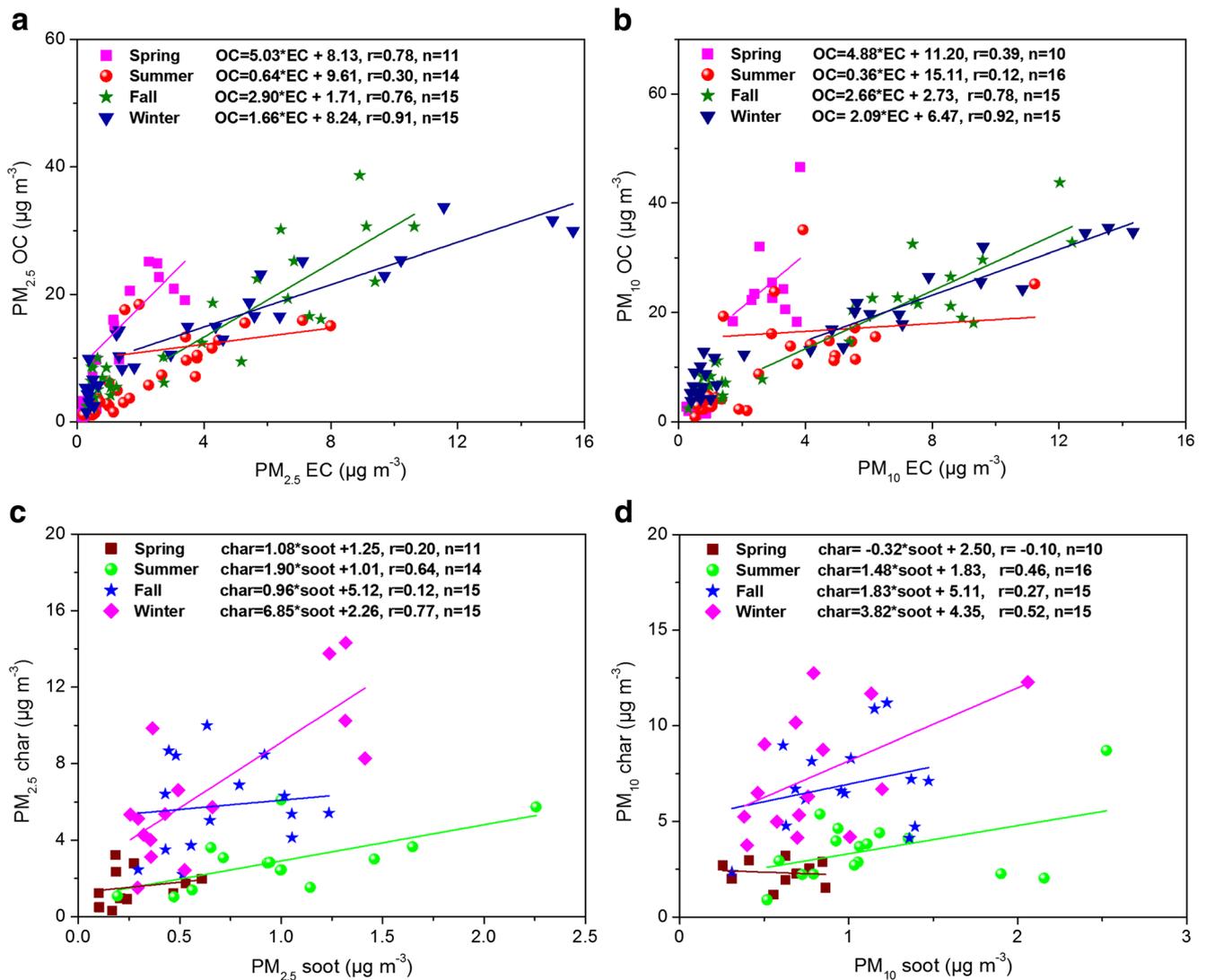
Fig. 3 Comparison of correlations between OC vs. EC and char vs. soot in $PM_{2.5}$ and PM_{10} in different seasons

Seasonal characteristics of OC/EC and char/soot ratios

OC/EC ratios are important indicators of the emission sources and transformation characteristics of carbonaceous aerosols. Studies have reported that a ratio of 1.1 is assumed for motor vehicle emission and 2.7 for coal combustion (Watson et al. 2001), while biomass burning shows a significantly high OC/EC ratio of 9.0 (Cachier et al. 1989). Cao et al. (2005) reported that the average OC/EC ratio in Xi'an was 1.6 for vehicular exhaust, 3.0 for coal combustion, and 12.3 for biomass burning. In addition to the indicated different emission sources, an OC/EC ratio exceeding 2.0 was usually regarded as an indication of SOC formation (Chow et al. 1996). The seasonal variation of average OC/EC and char/soot ratios is presented in Fig. 4. It can be seen that in both particle fractions, the OC/EC ratios were the highest in spring, indicating that biomass burning played a dominant role in particulate carbonaceous
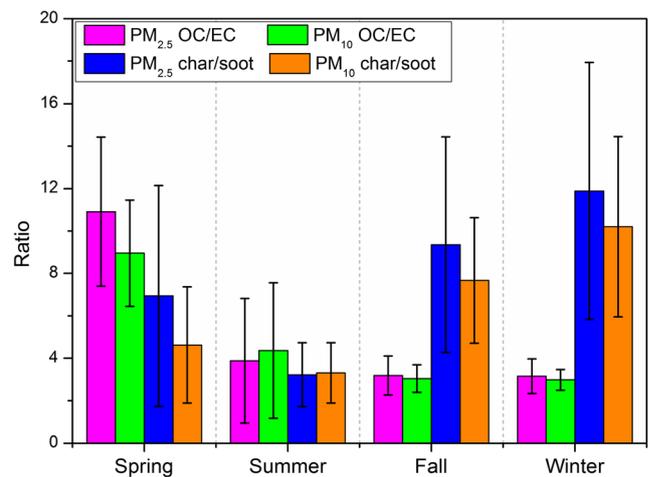
Fig. 4 Seasonal variations of OC/EC and char/soot ratios in $PM_{2.5}$ and PM_{10}

pollution in Huangshi. This is consistent with the finding that biomass burning typically got OC/EC ratios more than 7 or even higher (Fine et al. 2001; Zhang et al. 2007). Furthermore, regional contribution of aged aerosols with higher SOC levels also possibly helps to elevate the ambient OC/EC ratio (Cui et al. 2015). However, it is different from previous studies (Cao et al. 2005; Lonati et al. 2007; Pio et al. 2007), in which the individual average OC/EC ratio was found to be maximum in winter. This is due to emissions from biomass burning and coal combustion for domestic heating being usually higher in these areas in winter. Relatively higher OC/EC ratios were found in summer compared to those in autumn and winter, which possibly demonstrated the increased formation of secondary organic aerosols due to an enhancement of the photochemical reactions. In general, the mean values of OC/EC ratios in $PM_{2.5}$ and PM_{10} in other seasons were higher than 3.0, suggesting that the dominance of OC derived from various burning sources, such as coal combustion, traffic-related emissions, biomass burning, and SOC formation. Document data showed that about 16.66 million tons of coal was consumed for industrial production during 2006 to 2010 in Huangshi, and coal consumption accounts for 74.6% of the total energy consumption. This great consumption of coal resulted in heavy emission of volatile organic compounds (VOCs), which then resulted in more SOC formation through the year. During summer, autumn, and winter, the OC/EC ratios for $PM_{2.5}$ and PM_{10} sometimes lowered to < 3.0 (Fig. 4), possibly indicating the contribution from motor vehicle emissions.

The indicator of char/soot ratio was firstly reported by Han et al. (2009) to trace source profiles and successfully applied in several aerosol studies (Han et al. 2010; Kim et al. 2011b; Lim et al. 2012). According to several studies on combustion conditions (Chen et al. 2007; Chow et al. 2004; Han et al. 2010), motor vehicle emissions generally produce lower char/soot ratios, while coal combustion and biomass burning produces relatively higher char/soot ratios. However, the combustion conditions, such as fuel types (wood or grass, bituminous coal or anthracite coal, etc.), combustion mode (smoldering or flaming) and temperature, and moisture content, could also influence the char/soot ratios (Han et al. 2010). Seasonally, the char/soot ratios were ranked in the order of winter > fall > spring > summer for $PM_{2.5}$ and PM_{10} (Fig. 4). The relatively high char/soot ratios indicate that coal combustion and biomass burning significantly contributed to aerosol BC. This seasonal pattern is similar to the results observed in 14 Chinese cities (Han et al. 2009). Different from those cities in northern China, coal consumption in Huangshi is mainly for industrial manufacture but not for residential heating, because there are a large number of steel and smelting plants distributed everywhere. Furthermore, other enterprises, such as power plant, coking plant, and cement plant, also consume a lot of coal each year. The char/soot ratios in this study was higher than those found in Shanghai in summer of

2009 (Cao et al. 2013), in which motor vehicle exhaust seems an important emission source.

The characterization of eight carbon fractions

The contributions of eight carbon fractions to TC in $PM_{2.5}$ and PM_{10} have been plotted in Fig. 5. There were similar patterns among $PM_{2.5}$ and PM_{10} samples for carbon fraction contributions in each season. The most abundant carbon fractions were OC3 and OC4, followed by OC2, EC1-OP, and OP. OC1 and OP showed the highest contribution in spring, with the levels of 6.8 and 27.4% for $PM_{2.5}$, and 5.4 and 27.0% for PM_{10}, respectively. This indicated that biomass burning represented a significant contributor in the season. These ratios are higher than the 16.0 to 22.1% OP in TC found in Xi'an and the 8.0 to 17.8% OP in the Pearl River Delta Region in China. EC1-OP accounted for 7.7, 18.2, 22.0, and 22.7% of TC in $PM_{2.5}$ and 8.5, 17.0, 22.1, and 22.9% of TC in PM_{10} in spring, summer, autumn, and winter, respectively. These variations possibly suggested the increased contributions of coal combustion from spring to winter. The contributions of OC2, EC2, and EC3 were highest in summer both for $PM_{2.5}$ and PM_{10}, reflecting increased contributions from motor vehicle exhaust, especially the emissions of diesel vehicles.

Estimation of secondary organic carbon

The previous results have shown that most ratios of OC/EC exceeded 2.0 for both $PM_{2.5}$ and PM_{10} during the sampling period, indicating that there was production of secondary organic aerosols in both $PM_{2.5}$ and PM_{10}. Here, we used the EC tracer method to calculate the SOC concentrations in aerosols. According to the experiential equation suggested by Castro et al. (1999), the concentration of SOC could be calculated as follows:

$$SOC = TOC - EC \times (OC/EC)_{min}$$
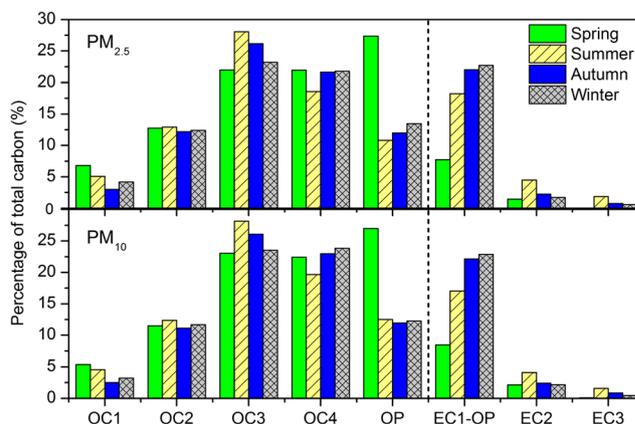
Fig. 5 The contributions of eight carbon fractions to TC in $PM_{2.5}$ and PM_{10}

where TOC is the total OC and $(OC/EC)_{min}$ is the minimum of the observed OC/EC ratios.

In the present study, SOC concentrations in $PM_{2.5}$ and PM_{10} ranged from 0.3 to 22.4 $\mu g\ m^{-3}$ and from 0.6 to 39.2 $\mu g\ m^{-3}$, respectively. The annual average concentration of SOC for $PM_{2.5}$ was 8.4 $\mu g\ m^{-3}$, accounting for 47.3% of OC concentrations and 8.0% of $PM_{2.5}$ mass. For PM_{10}, the average concentration of SOC was 10.0 $\mu g\ m^{-3}$, accounting for 45.4% of OC concentrations and 6.6% of PM_{10} mass (Table 3). This implied SOC was an important component of OC mass in two size fractions in Huangshi. The seasonal variations of SOC concentrations in $PM_{2.5}$ and PM_{10} were distinctly the highest in spring and the lowest in summer (Table 3), presenting a different trend with OC and EC. This observation contradicts with many other studies in the urban area. For example, in the studies of Cao et al. (2007) and Zhao et al. (2013), the SOC concentrations were higher in winter in several northern Chinese cities, which might be due to great coal consumption for resident home heating during winter, then causing enhanced emissions of primary carbonaceous particles and volatile organic gases and stimulating the formation of secondary organic aerosol (SOA), whereas there are some exceptions. Feng et al. (2009) and Gu et al. (2010) found that SOC concentration was higher during fall than in other seasons in Shanghai and Tianjin, respectively. Plaza et al. (2011) also detected that higher SOC contributed to OC concentrations related to increase in photochemical activity in spring and summer in Madrid. This different phenomenon may result from the distinct climatic condition.

Similar to the seasonal trends of SOC, the contribution of SOC to OC in $PM_{2.5}$ and PM_{10} were all higher in spring but lower in other three seasons (Table 3), indicating a low contribution of primary anthropogenic emissions. This pattern is different from many other Chinese urban sites where larger contribution of SOC to OC was generally found in fall and winter (Cui et al. 2015). It is thought that higher temperature in summer could facilitate the formation of SOC; however, the argument seems not applicable in our study. We expected that it was possibly due to a higher primary biogenic particle

influence during spring around the sampling site. It seems that SOC in the atmosphere was controlled by emissions (such as vegetation emitted organic aerosol) rather than temperature. The highest mass percentages of SOC for both $PM_{2.5}$ and PM_{10} occurred in spring and the lowest in winter (Table 3). The average percentages of SOC for $PM_{2.5}$ and PM_{10} were 8.0 and 6.6%, respectively, which were much lower than those measured in Hong Kong, Guangzhou, Shenzhen, and Zhuhai (Cao et al. 2003), but comparable to that for $PM_{2.5}$ in an urban site of Shanghai (7.8%, Feng et al. 2009). This indicated that SOC contributed a minor fraction of $PM_{2.5}$ and PM_{10} mass in Huangshi.

Source appointment of carbonaceous aerosols

Principal component analysis (PCA) has been applied for source appointment of carbonaceous aerosols in many studies (Cao et al. 2005; Li et al. 2012; Wang et al. 2015; Yang et al. 2005b). According to Cao et al. (2005), OC1 and OC2 represent biomass burning source and coal combustion, respectively; EC1, OC3, and OP indicate gasoline vehicle emissions. OC4 is enriched in the road dust profile (Chow et al. 2004). EC2 and EC3 reflect the contribution of diesel vehicle exhaust (Watson et al. 1994).

The PCA result of eight carbon fractions is shown in Table 4. For $PM_{2.5}$ samples, two principal components were identified in spring, summer, and fall, while only one principal component was identified in winter. Factor 1 in spring, which was responsible for 73.1% of the total variance, showed high loadings for OC1, OC2, OC3, OC4, EC1, EC2, and OP, suggesting the sources from biomass burning, coal combustion, motor vehicles exhaust, and road dust. Factor 2 (13.7% of the total variance) was highly loaded with EC3, representing the contribution from diesel vehicle exhaust. In summer and fall, two principal components were identified. Similar to the spring result, factor 1 in summer and winter reflects the contribution from coal combustion, gasoline vehicle emissions, and road dust, while factor 2 indicates diesel vehicle exhaust. In winter, just one principal component was identified, and

Table 3 Levels of secondary organic carbon (SOC) at Huangshi estimated from minimum OC/EC ratios

	SOC concentration ($\mu g\ m^{-3}$)		Percentage (SOC/OC, %)		Percentage (SOC/mass, %)	
	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}
Range	0.3–22.4	0.6–39.2	4.3–92.4	5.0–85.8	0.7–23.5	1.1–21.4
Spring	14.0	19.8	81.4	76.5	14.4	12.7
Summer	5.0	7.6	38.5	40.6	8.0	7.0
Fall	8.7	8.4	40.6	33.2	8.0	5.6
Winter	7.1	7.7	38.3	33.2	7.0	4.2
Annual average	8.4	10.0	47.3	45.4	8.0	6.6

Table 4 Factor loadings of principal component analysis (PCA) for eight carbon fractions in Huangshi

Species		Spring		Summer		Fall		Winter	
		F1	F2	F1	F2	F1	F2	F1	F2
OC1	$PM_{2.5}$	**0.834**	−0.298	0.629	− 0.332	0.641	0.529	**0.864**	0.065
	PM_{10}	**0.882**	− 0.081	0.603	− 0.355	0.508	0.632	**0.797**	
OC2	$PM_{2.5}$	**0.964**	− 0.150	**0.954**	− 0.174	**0.985**	− 0.080	**0.973**	− 0.376
	PM_{10}	**0.959**	0.213	**0.984**	0.077	**0.986**	− 0.048	**0.904**	
OC3	$PM_{2.5}$	**0.937**	− 0.195	**0.750**	0.391	**0.981**	− 0.092	**0.958**	− 0.188
	PM_{10}	**0.912**	0.279	**0.919**	0.207	**0.947**	− 0.159	**0.876**	
OC4	$PM_{2.5}$	**0.866**	− 0.415	**0.963**	0.034	**0.947**	− 0.104	**0.866**	− 0.100
	PM_{10}	**0.962**	0.090	**0.981**	− 0.049	**0.951**	0.007	**0.937**	
EC1	$PM_{2.5}$	**0.984**	0.087	**0.915**	− 0.157	**0.963**	− 0.073	**0.959**	− 0.200
	PM_{10}	**0.885**	− 0.145	**0.932**	− 0.084	**0.906**	− 0.175	**0.945**	
EC2	$PM_{2.5}$	**0.720**	0.445	0.558	**0.696**	0.171	**0.906**	**0.839**	**0.692**
	PM_{10}	0.111	**0.765**	0.538	**0.754**	**0.683**	0.350	0.619	
EC3	$PM_{2.5}$	0.453	**0.721**	0.353	**0.729**	− 0.017	**0.781**	**0.804**	0.633
	PM_{10}	− 0.397	**0.684**	0.044	**0.890**	0.035	**0.892**	**0.696**	
OP	$PM_{2.5}$	**0.950**	0.213	**0.714**	− 0.644	**0.927**	− 0.154	**0.921**	− 0.169
	PM_{10}	**0.885**	− 0.180	**0.872**	− 0.425	**0.855**	− 0.282	**0.786**	
Variance (%)	$PM_{2.5}$	73.1	13.7	57.2	21.8	63.2	22.1	81.0	14.3
	PM_{10}	64.9	15.5	63.2	21.6	63.1	18.2	68.5	

factor 1 (81.0% of the total variance) represents the mixed sources of biomass burning, coal combustion, road dust, and motor vehicle exhaust.

For PM_{10} samples, two principal components were identified in the four different seasons (Table 4). In spring, factor 1 was highly loaded by OC1, OC2, OC3, OC4, EC1, and OP, and explained 64.9% of the total system variance. This factor represents the sources from biomass burning, coal combustion, gasoline vehicle emissions, and road dust. Factor 2 was highly loaded by EC2 and EC3 and responsible for 15.5% of the total system variance, indicating the contribution from diesel vehicle exhaust. Similar to the result in summer for $PM_{2.5}$, factor 1 (63.2% of the total system variance) represents contribution from coal combustion and gasoline vehicle emissions, while factor 2 (21.6% of the total system variance) indicates the source from diesel vehicle exhaust. In fall, factor 1, which explained 63.1% of total variance, showed high loadings for OC2, OC3, OC4, EC1, EC2, and OP, representing the emissions from coal combustion and motor vehicle exhaust. Factor 2 (18.2% of the total system variance) was highly loaded by EC3, indicating diesel vehicle exhaust. In winter, factor 1 accounted for 68.5% of the total variance and had high loadings for OC1, OC2, OC3, OC4, EC1, EC3, and OP, indicating the contribution from biomass burning, coal combustion, and motor vehicle exhaust. Factor 2 which explained 14.3% of the total variance was highly loaded by EC2, reflecting the source from diesel vehicle exhaust.

In the present study, biomass burning seems an important source contribution to OC and EC in spring and winter for both coarse and fine particles. On an annual basis, emissions from industrial coal combustion, motor vehicle exhaust, and road dust are main sources for carbonaceous aerosol.

Typical haze-fog episode and possible sources

During the sampling period, a typical haze-fog episode occurred in Wuhan, Huangshi, and many other regions in Hubei province in central China on June 11, 2012. Some areas in the Yangtze River Delta, such as Nanjing, Wuxi, and Yangzhou, were also affected by this episode. Our monitoring data showed that the daily averaged $PM_{2.5}$ concentration in Huangshi reached 501.43 μg m^{-3}, exceeding the Chinese National Ambient Air Quality Standards of Class I (35 μg m^{-3}) (GB 3095-2012) by a factor of ~ 14 (Fig. S1). OC and SOC concentrations increased simultaneously and attained 127.61 and 117.88 μg m^{-3}, respectively (Fig. S2), which were approximately 7 and 14 times higher than the annual average levels, respectively. OC/EC and K$^+$/OC ratios were as high as 23.87 and 0.32, respectively (Fig. S3, S4), indicating the major contribution from biomass burning. The occurrence of the severe haze-fog episode could have resulted from transport of polluted regional air masses. This hypothesis was supported by the HYSPLIT backward trajectory (http://ready.arl.noaa.gov/HYSPLIT.php) simulation results (Fig. 6a) and MODIS fire records (Fig. 6b) observed with the Fire Information for Resource Management System (FIRMS) Web Fire Mapper (https://firms.modaps.eosdis.nasa.gov/firemap). As can be seen in Fig. 6b, extensive biomass burning activities occurred in northern Anhui, central Henan, and Shandong Province. Combustion of crop residues (e.g., corn and wheat) by the farmers resulted in sporadic emissions of biomass burning

Fig. 6 **a** HYSPLIT 48-h back air mass trajectories originating at the sampling site in Huangshi (30.21° N, 115.03° E) at 100, 500, and 1000 m above ground level every 6 h. **b** Regional distributions of fire counts (*red points*) map over China derived from MODIS observations during the period of 10–12 June 2012
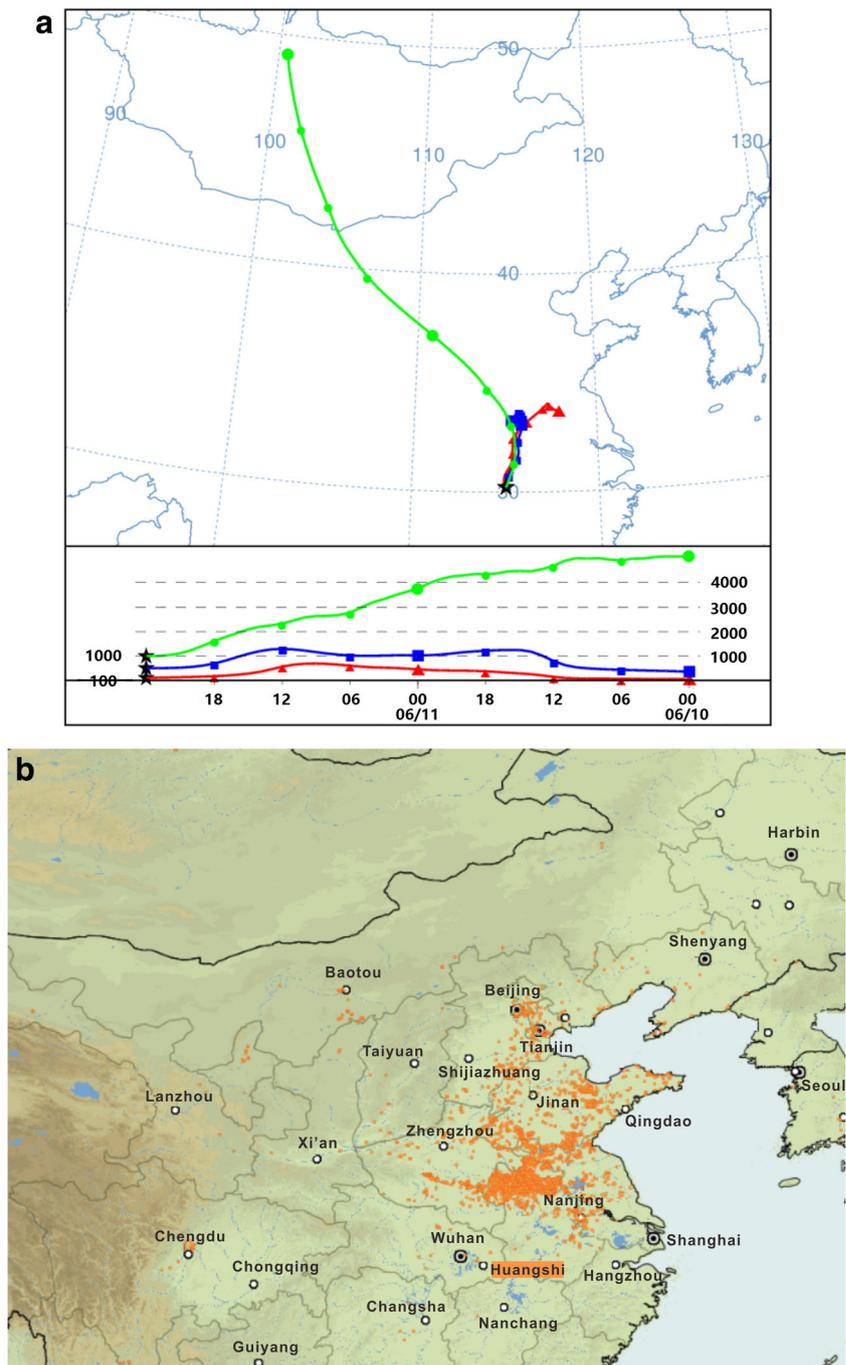
smoke. The trajectory from northerly flows transported the smoke to the middle reach of Yangtze River.

Conclusions

The $PM_{2.5}$ and PM_{10} pollution characteristics and carbonaceous components were investigated at Huangshi, central China. Annual average $PM_{2.5}$ and PM_{10} concentrations were 104.90 and 151.23 $\mu g\ m^{-3}$, respectively, indicating the serious pollution of particulate matter in Huangshi. OC and EC were at quite high levels with mean values of 17.85 and 5.15 $\mu g\ m^{-3}$ for $PM_{2.5}$, and 22.03 and 6.20 $\mu g\ m^{-3}$ for PM_{10}. OC and EC were the dominant species in $PM_{2.5}$, which account for 17.01 and 4.91% of $PM_{2.5}$, respectively. $PM_{2.5}$ and PM_{10} and carbonaceous species were generally found to be higher during winter and lower during summer. However, char and soot concentrations showed different seasonal patterns. The observed positive correlations between OC and EC during fall and winter for $PM_{2.5}$ and PM_{10} suggested the

contributions of common sources, while poor correlations of
OC and EC during spring and summer were likely due to
difference in atmospheric process and changes in emission
sources. The averaged OC/EC and char/soot ratios were 5.11
and 4.46 for $PM_{2.5}$, and 7.96 and 6.56 for PM_{10}. This indicat-
ed significant contribution from biomass burning smoke and
coal combustion emissions. The annual average SOC concen-
trations were 8.38 and 10.0 μg m^{-3} for $PM_{2.5}$ and PM_{10},
respectively, accounting for 47.33 and 45.38% of OC concen-
trations, respectively, suggesting that SOC was an important
component of OC mass in Huangshi. The typical haze-fog
episode was possibly attributed to biomass burning emissions
transported from the adjacent regions.

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