



Characteristics and Sources of Black Carbon in Atmospheric Dustfall Particles from Huangshi, China

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ABSTRACT

Concentrations of carbonaceous particles in atmospheric dustfall particles in Huangshi, an industrial city in central China, were determined using a thermal-optical reflectance method. The black carbon (BC) contents in ninety-five dustfall samples ranged from 4.3 to 64.9 g kg⁻¹ with an average of 17.0 g kg⁻¹. These values were higher than those in world background soils and demonstrated serious contamination of the environment in this city. Overall, BC accounted for 17.6–71.3% (mean: 42.0%) of the organic carbon (OC), and BC and OC were positively correlated ($r^2 = 0.90$). Average char and soot contents were 8.01 g kg⁻¹ and 8.65 g kg⁻¹, respectively, and char/soot ratios ranged from 0.28 to 1.97 with an average of 1.01. All the measured carbonaceous species positively correlated with each another, suggesting their common sources. BC, char, and soot showed large spatial distribution variability, with high levels of BC adjacent to the presumed emission sources, such as a power plant and railway line. Analyses of BC/OC and char/soot ratios indicate major impacts from fossil fuel combustion, especially motor vehicle emissions and coal combustion. Industrial dusts related to coal use appear to be the major contributor to BC in dustfall, and this is likely related to the extensive industrial activities in the city, including metal smelting.

Keywords: Black carbon; Dustfall; Char; Soot; Sources.

INTRODUCTION

Black carbon (BC), a product of incomplete combustion of biomass and fossil fuels, is not a single chemical compound but rather a “combustion continuum” (Goldberg, 1985; Masiello, 2004). Ubiquitous in the earth system, BC has been found in water, soils, atmosphere, ice, and sediments (Schmidt and Noack, 2000). As it is largely composed of condensed aromatic rings with few functional groups, BC is generally considered chemically recalcitrant. However, it

plays a significant role in the global carbon cycle, and has potential to impact climate change (Kuhlbusch and Crutzen, 1995; Ramanathan and Carmichael, 2008).

The combustion continuum of materials produced by fires ranges from slightly charred plant matter to highly refractory, graphitized soot (Masiello, 2004). Among these products, char and soot are two of the important sub-groups of BC: char forms at lower temperatures than soot, and char particles, which range in diameter from 1 to 100 μm, are larger than soot. As combustion residuals, char retains some recognizable morphological features of the source materials. In contrast, soot forms at higher temperatures when hydrocarbons from the gas phase condense, which results in the formation of primary particles typically cluster together into agglomerates of 0.1 to 1 μm in size, smaller than those of char (Elmquist *et al.*, 2006). As a result of their different formation mechanisms, these two BC species differ in physical and chemical properties (Han *et al.*, 2010). Thus, new insights into the characteristics of the fires can be

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obtained by measuring char and soot simultaneously, and such measurements have made it possible to distinguish between emission sources (Han *et al.*, 2009).

Most BC quantification methods intentionally or inadvertently detect a particular form of BC, and few studies have distinguished char from soot. One consequence of this is that several inter-comparisons of BC involving different quantification methods for various types of materials (aerosols, soils, dusts) have shown quite discrepant results (Schmidt *et al.*, 2001; Hammes *et al.*, 2007), part of which can be explained by differences in the BC fractions that were quantified. Recently, a thermal-optical reflectance (TOR) method, which had been used to quantify BC in aerosols, was used to simultaneously measure char and soot. TOR method has been applied for source identification studies involving soils, dusts, and aerosols (Han *et al.*, 2009, 2010; Kim *et al.*, 2011). The development of the TOR char/soot differentiation scheme provides new and useful information that also can be applied to studies of the effects of BC on climate and the environment.

In the past few decades, a large number of BC-related studies have been conducted, mainly focusing on BC concentrations and storage in soils, sediments, waters, atmosphere, and ice cores (Masiello and Druffel, 1998; Mitra *et al.*, 2002; Czimeczik *et al.*, 2003; Cao *et al.*, 2005; Xu *et al.*, 2009). BC particles, in combination with various toxic chemicals in the atmosphere (e.g., heavy metals or organic pollutants) can deposit as road dusts and in soils, waters, and sediments through dry and wet deposition. Although the dustfall particles are large, often with diameters of $\geq 10 \mu\text{m}$, they can be resuspended, a process that leads to continuing contamination of the environment.

With references to atmospheric dustfall studies, heavy metals (Farfel *et al.*, 2003; Das *et al.*, 2005), polycyclic aromatic hydrocarbons (PAHs) (Wei *et al.*, 2015), magnetic and mineralogical properties (Xia *et al.*, 2008), and chemical composition (Zdanowicz *et al.*, 2006) have all been extensively investigated. However, little is known about BC in atmospheric dustfall, and few if any studies have measured char and soot in dustfall. This limits our understanding of the pollution by carbonaceous particles and the contributions of different sources to BC in dustfall. Therefore, in the present study, we used the TOR method to determine the concentrations of three carbonaceous species (BC, char and soot) in atmospheric dustfall samples collected in Huangshi, an industrial city in central China. The main objectives of the study were (1) to assess the levels of BC, char, and soot in dustfall samples; (2) to characterize the spatial distributions of these carbonaceous particles; (3) to investigate possible relationships between the selected carbonaceous species; and (4) to identify likely sources of BC particles in an urban environment and test the feasibility of using BC/OC and char/soot ratios as tools for identifying these sources.

MATERIALS AND METHODS

Study Area

The study area and location of the sampling site in Huangshi (E114°31'–115°30', N29°30'–30°15') are shown

in Fig. 1. Huangshi is the second largest city in Hubei province and is located in the eastern part of the province along the Yangtze River. It covers an area of 4,583 kilometers and is home to ~2.6 million of people. It is an important industrial base for raw materials in central China, and as such, the city has long-standing industrial culture, and is known as the “Hometown of Bronze” and “Cradle of Steel”. It is the largest mining city of the province and accounts for 26% of the gross production of the mining industries in the whole province (Yu *et al.*, 2005). Huangshi has a typical sub-tropical continental monsoon climate, with a mean annual temperature of 17°C and a mean precipitation amount of 1382.6 mm. The number of motor vehicles was estimated to be over 284,000 at the end of March 2012.

Sampling

A total of ninety-five dustfall samples were collected during May 2012. These ninety-five sampling sites are distributed in different functional zones, including industrial area, traffic lines, cultural and educational district, commercial district, residential area, and suburb. Because of the severe pollution of industrial dust and fugitive dust in Huangshi, the sampling sites located near the typical emitters, such as iron and steel plant, smelting plant, cement plant, thermal power plant and important traffic lines, were paid more attention. These sampling sites are believed to be representative of the entire city due to the high density of sampling sites. Each sample was collected with a brush from the surface of wooden windowsill or telegraph pole which was ~1.5 m above ground level. The collected samples were weighed and then stored in glass jars. All the dustfall samples were air dried and sieved to remove any particles larger than 1-mm, then ground and homogenized using an agate mortar, and finally processed with a 63- μm sieve. After homogenization, the samples were again dried at 40°C and placed in an air-tight container for storage.

Chemical Analysis

BC Determinations

We used the acid pretreatment method developed by Han *et al.* (2007a) to extract BC from the samples. Briefly, each sample was first pretreated with HCl to remove carbonate, then digested with a mixture of HCl and HF to eliminate silicates, followed by a treatment with HCl to remove residual fluorite and carbonate. Finally, the remaining residue was rinsed and filtered through a pre-fired (850°C, 3 h) 47 mm quartz filter prior to BC instrumental analysis.

We measured BC content in each dustfall sample using thermal-optical reflectance method (TOR). The analysis was carried out with using a Desert Research Institute (DRI) Model 2001 Carbon Analyzer (Atmoslytic Inc., Calabasas, CA) following the IMPROVE protocol (Chow *et al.*, 1993; Cao *et al.*, 2005). Briefly, a 0.526 cm² punch of a sample quartz filter was subjected to a stepped temperature program (120°C, 250°C, 450°C, and 550°C) in a flow of non-oxidizing He atmosphere, which produced four organic carbon (OC) fractions (OC1, OC2, OC3, and OC4). The next step was the oxidation of the residual carbon in a flow of 2% O₂/98% He with temperature steps at 550°C, 700°C, and 800°C,

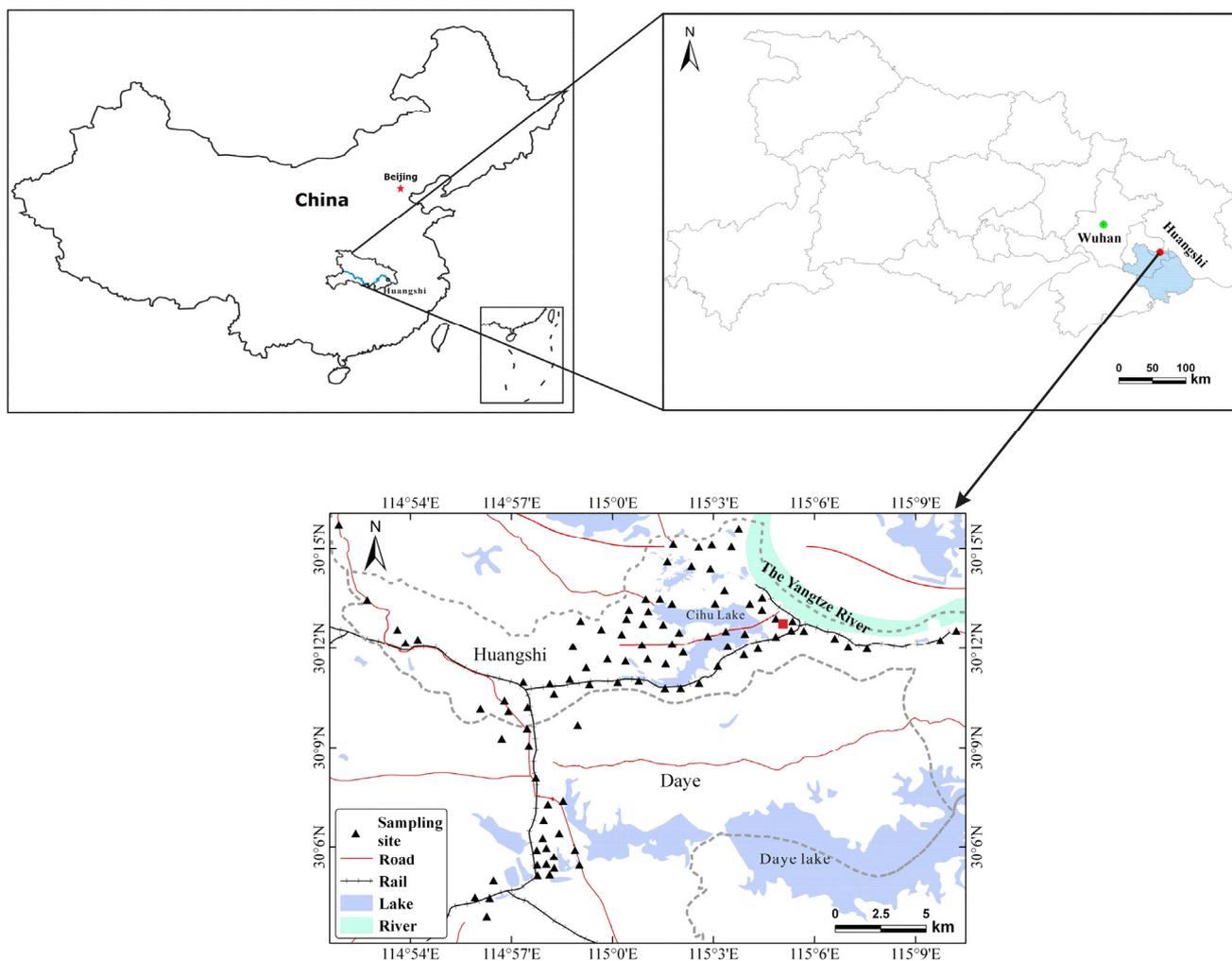


Fig. 1. Locations of the study area and sampling sites at Huangshi, China.

which produced three elemental carbon (EC) fractions (EC1, EC2, and EC3), respectively. At the same time, pyrolyzed organic carbon (PyOC) was produced in the inert atmosphere, which decreased the reflected light to correct for charred OC. More detailed information about the IMPROVE_TOR method can be found elsewhere (Cao *et al.*, 2006; Han *et al.*, 2010). In this study, char was EC1 minus PyOC; soot was the sum of EC2 and EC3; and BC was the sum of char and soot (Han *et al.*, 2007b).

Organic Carbon Analysis

Organic carbon in the dustfall samples was determined after pretreatment of the samples with HCl to remove carbonate carbon (Ryba and Burgess, 2002). Analyses were performed in duplicate via dry combustion (975°C) using a Vario EL II analyzer (Elementar Analysensysteme, Hanau, Germany). The detection limit for carbon was 0.4 µg.

Statistics and Analysis

Replicate analyses for this study were performed at the rate of one per group of 10 samples. Quality assurance and quality control procedures for the carbon analysis were described in detailed by Cao *et al.* (2006). Correlation

analyses were performed using SPSS 19.0 (Statistical Product and Service Solutions, SPSS Inc., USA). The derived correlation coefficients were starred when the correlation was significant at either of two probability (*p*) levels ($p < 0.01$ and $p < 0.05$). Two data mapping software packages were used—ArcGIS desktop 10.0 (ESRI, Redlands, CA, USA) and Origin 8.5 (OriginLab, Northampton, MA).

RESULTS AND DISCUSSION

Carbonaceous Particles in Atmospheric Dustfall

BC concentrations in the dustfall samples varied greatly, ranging from 4.34 to 64.9 g kg⁻¹, with a mean value of 17.0 g kg⁻¹ (Table 1). The median BC content was 14.0 g kg⁻¹ with a coefficient of variation (CV) of 68.3%. The BC concentrations in the samples from Huangshi were higher than those in dustfall from Beijing (1.21–50.1 g kg⁻¹, Tang *et al.*, 2013) or Northwest Africa (2.4 g kg⁻¹, Eglinton *et al.*, 2002). The possible reason is that the history of the dustfall particles in these three studies is different. The dustfall in our study is from a long-term deposit with accumulated BC while the results conducted in Beijing and Northwest Africa just collected samples in months or last for several months.

Table 1. Statistical summary of carbonaceous particle concentrations (g kg^{-1}) and BC/OC and char/soot ratios in atmospheric dustfall from Huangshi.

Statistic	Mass concentration (g kg^{-1} dry weight)				BC/OC (%)	Char/Soot ratio
	OC ^a	BC ^a	Char	Soot		
Minimum	11.00	4.34	1.39	2.01	17.6	0.33
Maximum	107.1	64.9	33.1	31.8	70.3	1.81
Median	34.4	14.0	6.71	6.63	41.5	1.06
Mean	39.6	17.0	8.44	8.53	42.0	1.04
SD ^b	20.2	11.6	5.97	6.01	11.4	0.34
CV ^c (%)	51.0	68.3	70.7	70.5	27.1	32.4

^aOC and BC stand for organic carbon and black carbon, respectively.

^aSD indicates standard deviation.

^bCV indicates coefficient of variation.

Moreover, the average BC content appeared to be much higher than those in urban soils (He and Zhang, 2009; Liu *et al.*, 2011) and road dusts (Han *et al.*, 2009). Different rates of BC input should be largely responsible for the higher BC contents observed in this study, although differences in analytical methods might have caused a portion of the disparities (Hammes *et al.*, 2007). As further discussed below, the high BC concentrations found in this study were most likely related to the extensive industrial activities in Huangshi.

The average OC content of the dustfall samples was 39.6 g kg^{-1} , which is much higher than what has been reported for dustfall samples from Northwest Africa (10.2 g kg^{-1} , Eglinton *et al.*, 2002). This is likely due to the fact that the upper continental crust was the main source for the Northwest African dust, and much of the carbon in those samples was likely old carbon. In contrast, the main source for the urban dustfall in this study was more likely industrial dust and fugitive dust from road traffic and construction; and as a result, a significant fraction of the organic carbon content was likely from recent emissions. Interestingly, the level of OC in the Huangshi dustfall was higher than those reported for soils from several megacities, including Delhi, Phoenix, Nanjing, and Beijing (He and Zhang, 2009; Agarwal and Bucheli, 2011; Liu *et al.*, 2011; Hamilton and Hartnett, 2013). Effective land-use and management practices may have limited the labile carbon in certain urban soils, thereby lowering the OC concentrations. Further studies are needed to confirm this hypothesis.

The char and soot concentrations ranged from $1.39\text{--}33.1 \text{ g kg}^{-1}$ and $2.01\text{--}31.8 \text{ g kg}^{-1}$, with mean values of 8.44 g kg^{-1} and 8.53 g kg^{-1} , respectively. These levels were much higher than those for road dusts from Xi'an, China measured by the same TOR method (Han *et al.*, 2009). Compared with the Xi'an road dusts, the average concentrations of char and soot in the Huangshi dustfall were about 2 and 3 times higher, respectively. Several studies also have shown high concentrations of char and soot in atmospheric aerosol particles from heavy traffic roads or tunnels (Zhu *et al.*, 2010). Both char and soot mainly come from fossil fuel combustion, and in urban areas, motor vehicles emissions are especially important. Furthermore, coal combustion for residential and industrial uses may be another great emission sources (Ramanathan and Carmichael, 2008). Therefore, the char and soot data indicate that the pollution levels in Huangshi

are quite high.

The TOR data showed that BC in the dustfall accounted for 17.6% to 70.3% of the OC, with an average of 42.0%, a percentage considerably higher than what was reported for dust samples from northwest Africa (Eglinton *et al.*, 2002), but a little lower than that in German chernozemic soils (Schmidt *et al.*, 1999). The high percentage of BC to OC in the dustfall from Huangshi was comparable to that in urban soils from Stuttgart, Germany (73%, Lorenz *et al.*, 2006). These high ratios of BC/OC indicate that dustfall in industrialized urban regions may contain substantial amounts of anthropogenic organic matter, and that a significant proportion of the OC in those areas is recalcitrant BC.

The atmospheric dustfall had widely variable char/soot ratios, ranging from 0.33 to 1.81 (median = 1.06, arithmetic mean = 1.04), slightly lower than the ratio reported for Xi'an road dusts (average 1.66, Han *et al.*, 2009). Knowing that the ratio of char/soot differs markedly between different primary emission sources, the findings here indicated the variety of emission sources impacting the various sampling sites.

Spatial Distributions of Carbonaceous Particles

Fig. 2 shows that the spatial variations of BC concentrations reached to more than ten-fold. Generally, high BC values were found along the Yangtze River and the east-west railway, which is in good agreement with observations by Han *et al.* (2009) and Lorenz *et al.* (2006) and can be explained by emissions from the diesel engines commonly used to power the trains. Another possible reason for the high BC along the railway is motor vehicle emissions because a road adjacent to the railway is used by heavy trucks. On the other hand, low BC values were found along the south-north railway in Daye city, and this result appears to be in conflict with the elevated BC along the east-west railway. The reason for the different finding is that the east-west railway usually has freight-train loaded with different kinds of coal and powered by diesel engine, while the south-north railway always runs inter-city train powered by electricity.

In any case, it is likely that the spatial variability reflects local emissions in many instances because the sampling sites adjacent to a thermal power plant showed high BC accumulations. This is almost certainly related to coal combustion at the power plant because coal burning produces large quantities of carbonaceous particles, including OC,

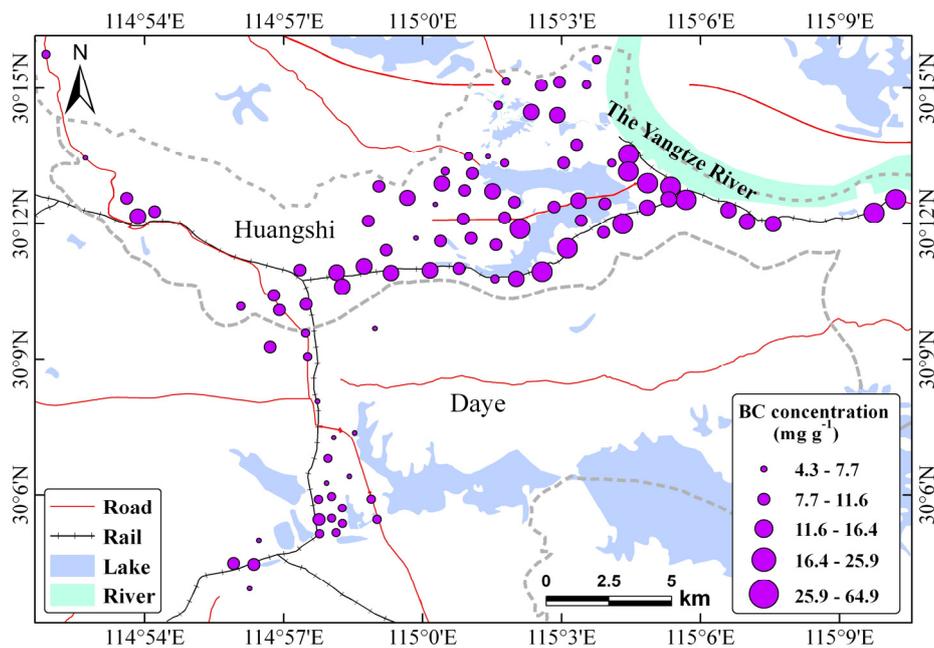


Fig. 2. Black carbon (BC) concentrations at the sampling sites.

BC, and a variety of other compounds (Zhang *et al.*, 2008). However, this conclusion seems to be at odds with the results of Koschke *et al.* (2011) who found that sites with organic-rich humic (Oa) layers close to the power plants had low soil BC contents. This was explained by the deposition of fly-ash particles which reduced the relative amount of BC in soils.

In our study, high concentrations of BC were found in the eastern part of Huangshi, which is the main urban zone of the city and a hub for various human activities—it also contains a cement plant, a wharf, a thermal power plant, many heavily trafficked roads and city villages. As a result, BC emissions from motor vehicles, diesel engines on ships, and industrial and residential coal use in eastern Huangshi likely produced more contaminated dusts compared with the western part of the city. Along these lines, Lehndorff *et al.* (2015) found that BC emissions from fossil fuels contributed 75% to the total BC in arable soils of Hall, Germany where coal use was the predominant source. According to statistics compiled by Huangshi Development and Reform Commission (http://www.hsfgw.gov.cn/xxgk/zfxgkml/fzghjndjh/qsgmjjshfzgh/201309/t20130918_157748.html), coal accounts for 74.6% of the energy used in Huangshi; and therefore, one may conclude that BC loadings will remain high as long as coal is the primary source of energy.

The accumulation of char was high along the east-west railway and in the eastern part of Huangshi (Fig. 3). The distribution pattern of soot was similar to that of char (Fig. 4), most likely due to the emissions of both species from coal combustion and vehicle exhausts. Indeed, the peak concentrations of both char and soot were found near the ferry and thermal power plant. Char particles whose sizes are typically $< 100 \mu\text{m}$ travel relatively short distances and tend to deposit near the fire sources (Whitlock and Larsen, 2002). Submicron soot particles, in contrast, can remain suspended in the atmosphere for several months and travel

great distances before being deposited (Ogren and Charlson, 1983). Therefore, in addition to impacts of the local emissions, soot particles from long-range transport may be another source for the soot in dustfall, but this evidently was not a major effect because the distributions of char and soot were similar.

Correlations of Carbonaceous Particles

As shown in Table 2, all measured carbonaceous particles in the dustfall samples were positively correlated with one another. Positive correlations between OC and BC previously have been found for soils, sediments, and urban dusts (Middelburg *et al.*, 1999; Huang *et al.*, 2012; Zhan *et al.*, 2013). One possible cause for these types of relationships is that BC particles have large surface area to volume ratios and many nanopores (Cornelissen *et al.*, 2005), which leads to a high sorption capacity. As a result BC tends to adsorb polycyclic aromatic hydrocarbons (PAHs) and other planar compounds that are produced along with BC during the incomplete combustion of organic matter, including fossil fuels, biomass, and industrial wastes (Glaser *et al.*, 2005). In our particular case, most of the sampling sites were located adjacent to industrial plants, residential areas or near roads, and therefore organic compounds from anthropogenic sources probably adsorbed to the BC particles and deposited in those regions. Furthermore, this positive correlation suggests that OC and BC may originate from common sources and that BC may increase both the concentrations and the retention of OC in dustfall.

There also were strong positive correlations between OC versus char and OC versus soot, indicating that dustfall rich in OC may contain relatively large amounts of pyrogenic C, but we hasten to caution that this finding may not necessarily be valid for other study areas. Char and soot can form simultaneously during combustion even though their

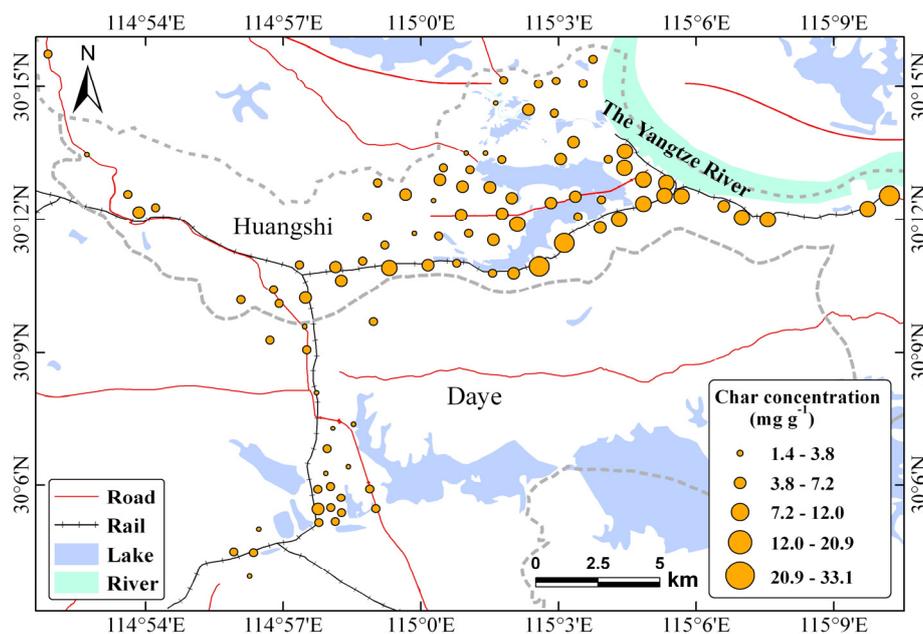


Fig. 3. Char concentrations at the sampling sites.

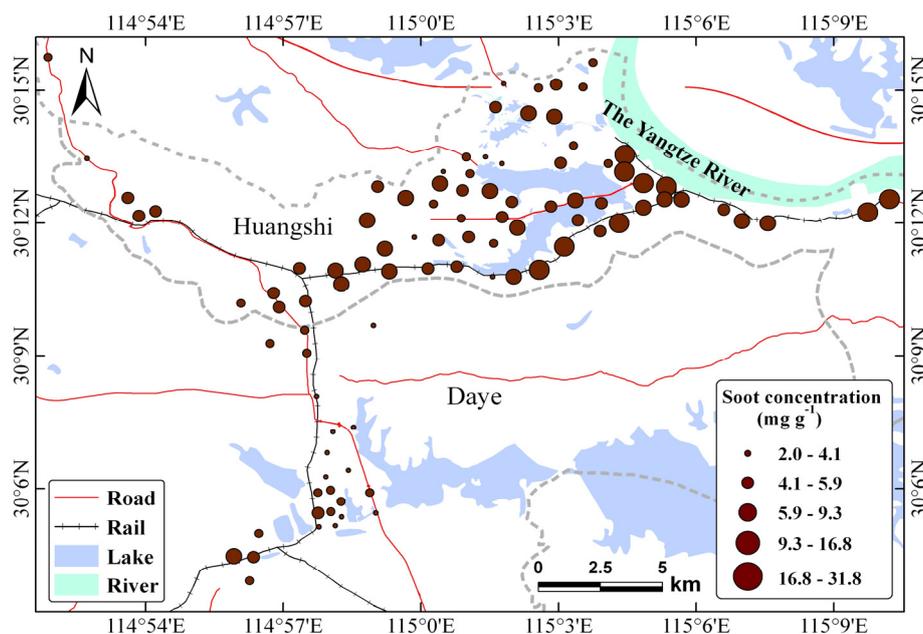


Fig. 4. Soot concentrations at the sampling sites.

Table 2. Pearson's correlation matrix for the carbonaceous particles concentrations of atmospheric dustfall.

	OC	BC	Char	Soot
OC	1			
BC	0.88**	1		
Char	0.82**	0.92**	1	
Soot	0.83**	0.95**	0.77**	1

** Correlation significant at the $p < 0.01$ level.

formation mechanisms are quite different (Hammes *et al.*, 2007), and this may explain the strong correlations for BC

with char and soot ($r^2 = 0.92$ and $r^2 = 0.95$, respectively, both $p < 0.01$). This finding is in good agreement with an urban dust study conducted in Xi'an by Han *et al.* (2009) who found that char and soot accounted for 60% and 40% of BC, respectively, and who also reported significant correlations between BC, char, and soot.

The char and soot concentrations themselves also were strongly correlated ($r^2 = 0.77$, $p < 0.01$), which suggests that the two species co-accumulated in the dustfall and may have been produced by the same emission sources. Generally, char forms from the combustion of organic matter or directly from pyrolysis, and it retains some morphological features

of the original fuel particles; soot on the other hand is formed at higher temperatures via gas-to-particle conversion processes so these particles differ as a function of the fuels burned (Han *et al.*, 2010). In addition to soot emissions, the combustion of liquid fuels (e.g., gasoline, diesel) is another possible source for char as a result of inefficient combustion at low temperatures or in poorly tuned vehicles (Moldanová *et al.*, 2009). Therefore, motor vehicles can be significant sources for both char and soot, especially in urban areas, and this is another possible reason for the observed correlation between char and soot in dustfall.

BC Sources

Previous studies have shown that biomass burning was the major source for BC in soils of forest systems and grasslands (Czimczik *et al.*, 2003; Ohlson *et al.*, 2009). Whereas in urban areas, fossil fuel combustion may be a more important source for BC in soils (Han *et al.*, 2009; He and Zhang, 2009; Agarwal and Bucheli, 2011; Liu *et al.*, 2011). For example, Agarwal and Bucheli (2011) found that BC concentrations in Delhi soils were significantly higher at traffic and industrial sites than at remote sites, indicating probable impacts from fossil fuel combustion. Similarly, Liu *et al.* (2011) examined BC concentrations in soils from urban and rural areas of Beijing, and they suggested that BC in urban soils mainly came from fossil fuel combustion, especially traffic emissions.

Several studies have reported that BC/OC ratio in aerosols varied significantly among sources, and it has been suggested that a BC/OC ratio of 0.11 ± 0.03 is indicative of biomass burning while a ratio of 0.5 ± 0.05 is more characteristic of fossil fuel combustion (Novakov *et al.*, 2000). The ratio of BC/OC also has been used for source appointment studies of soils (He and Zhang, 2009). The average BC/OC ratio in the Huangshi dustfall was ~ 0.42 , which is close to the values observed in urban soils from Beijing (0.37, Liu *et al.*, 2011) and Nanjing (0.44, He and Zhang, 2009), suggesting fossil fuel combustion, in particular coal use and vehicle exhaust, was responsible for the high BC/OC ratios. This finding is consistent with aerosol BC studies by Dan *et al.* (2004) who found that the BC/OC ratio in Beijing averaged 0.41 in winter and further concluded that coal combustion was a dominant source for carbonaceous particles. The BC/OC ratio in our study was higher than that in carbonaceous PM_{2.5} from Xi'an, China (0.23, Han *et al.*, 2010) but slightly lower than at a roadside site in Saitama, Japan (0.54, Kim *et al.*, 2011). The differences in the BC/OC ratios at these sites can be attributed to the differences in the amounts and types of fossil fuels burned. As can be seen from Fig. 5(a), $\sim 43\%$ of sampling sites had BC/OC ratios ranging from 0.1 to 0.4, revealing impacts from both biomass burning and fossil fuel combustion, but the contribution of biomass burning evidently was relatively high because these values were closer to the ratio characteristic of biomass source. Some of the BC/OC ratios were very high, higher even than the ratio of 0.5, which is the reference value for fossil fuels.

Char/soot ratios similarly have been used as indicators of emissions and for source appointments involving both soils (Han *et al.*, 2009) and aerosols (Han *et al.*, 2010). According to Han *et al.* (2010), different fuel types, such as biomass

burning, coal combustion, vehicle exhaust, and cooking produce distinctly different char/soot ratios. Generally, the char/soot ratios are lower for motor vehicle exhausts and grass burning, but higher for wood combustion, particularly when biomass smoldering at low temperature (Chow *et al.*, 2004; Chen *et al.*, 2007). The ratio resulting from coal combustion is variable and may be extremely low or relatively high, depending on the type of coal (bituminous or anthracite) burned (Han *et al.*, 2010).

In this study, the char/soot ratios ranged from 0.33–1.81 and averaged 1.04 (Table 1), all of which are lower than the ratio of 1.9 for coal combustion (Cao *et al.*, 2005) and much lower than the ratio for biomass burning (Chow *et al.*, 2004). The dustfall char/soot ratio was higher than that for diesel exhaust (0.3) or for gasoline emissions (0.7) (Cao *et al.*, 2006). These comparisons indicate that the main sources for BC were coal combustion and motor vehicle emissions, and this is consistent with the discussion above concerning the analysis of BC/OC ratios.

Char/soot ratios > 1.0 accounted for $\sim 60\%$ of the study data (Fig. 5(b)), and this indicates a significant contribution from coal combustion to the regional dustfall BC. The heavy concentration of coal-burning industries in Huangshi (e.g., coal-fired power plants, cement plants, steel plants, and smelters, etc.) can explain these results. Furthermore, there are numerous, widely distributed, coal-mining plants, and this multitude of coal-related sources can help explain the observed high char/soot ratios. Approximately 40% of the dustfall samples had char/soot ratios lower than 1.0 (Fig. 5(b)), implying strong influences of motor vehicles around certain sampling sites.

Overall, the contribution of BC from biomass burning appears to be substantially less than from coal as few if any of the char/soot ratios approached the values diagnostic for the biomass source. This observation seems to contradict the results obtained through the analyses of BC/OC ratios, which indicated that emissions from biomass burning were important for dustfall BC, at least in some regions. Although both char and soot particles can be transported from other surrounding areas, it is possible that the influence of transport on char/soot ratios was small, and therefore, local emissions were the main contributors to BC.

From a larger perspective, both the BC/OC and char/soot ratios are potentially useful for identifying likely sources for BC in dustfall, and our findings not only support the usefulness of BC/OC ratios for source identification (He and Zhang, 2009; Novakov *et al.*, 2000) but also the scheme for differentiating char and soot developed by Han *et al.* (2009, 2010). However, the comparisons of these two indicators in different types of environmental media (e.g., soils, sediments, and aerosols) should be undertaken with caution because the characteristic ratios may not be applicable for all situations. For example, a study conducted on a paleosol-loess sequence in Luochuan, China showed that char/soot ratios are < 1.0 at the depth of 160–240 cm, which corresponds to an age of $\sim 16,000$ – $21,000$ a (Han *et al.*, unpublished data). If one was to interpret the char/soot ratios using the typical modern ratios shown above, one would conclude that the main source of BC during that

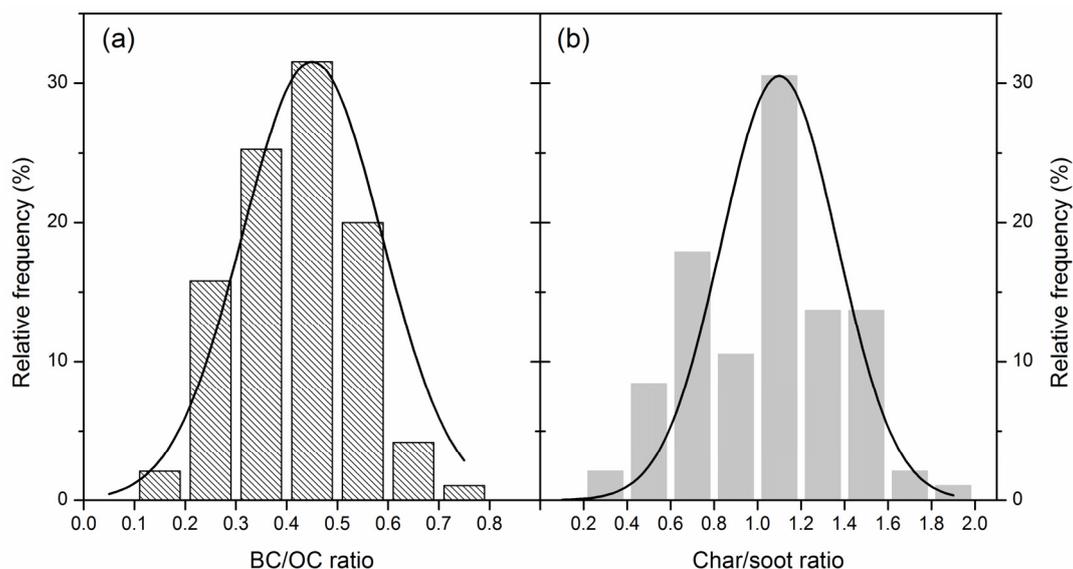


Fig. 5. Frequency distributions of the BC/OC and char/soot ratios in atmospheric dustfall from Huangshi.

period was fossil fuel combustion. This conclusion would not correspond with the facts, however, because fossil fuel combustion could not have been a major source for BC tens of thousands of years ago. Moreover, the terrain, climate, and locations of the study areas are all likely to influence the quantities and types of BC particles delivered by long-range transport, and therefore these factors, too, could affect the mass ratios of carbonaceous species.

BC Deposition and Environmental Implications

Generally, one might expect that fossil fuel combustion would be the primary source for BC in dustfall from Huangshi, but the main type of BC that accumulated in this area appears to be char not soot, the latter being the more refractory and condensed BC fraction. Char/charcoal evidently was a major component of soil BC in some areas because even though biomass burning is usually its most important source, coal combustion and diesel engines also can emit char through incomplete combustion. Thus, it is likely that industrial emissions, especially those from coal-powered metal smelters in Huangshi, led to high accumulation rates for fossil BC over the past several decades. This type of influence can be seen in the historical variations of char/soot ratio in sediments from Lake Chaohu, eastern China (Han *et al.*, 2011). Moreover, exhaust emissions from motor vehicles can lead to high BC deposition rates in urban areas—this has been shown in studies of both aerosols and sediments. For example, by using the TOR method, Han *et al.* (2011) found that the variations of soot in the sediments from Lake Chaohu increased after 1978, corresponding with the growth in the total number of motor vehicles.

The quantities of BC deposited are affected by many factors, including emission sources (biomass burning, fossil fuel combustion or erosion of geologic materials), transport mode (atmospheric or fluvial), climatic conditions, and proximity to the emitters. Some studies have reported BC deposition rates for different environmental types of environmental media. Sánchez-García *et al.* (2012) found

that the soot deposition rate reached $1 \text{ g m}^{-2} \text{ yr}^{-1}$ for recent European shelf sediments, and more recently, Lehnendorff *et al.* (2015) reported that from 1958–1971 the input of industrial BC deposition to arable soils from Halle, Germany was $9 \text{ g m}^{-2} \text{ yr}^{-1}$. Tang *et al.* (2013) observed that the mean deposition of BC for atmospheric dustfall in Beijing was $1.20 \text{ g m}^{-2} \text{ yr}^{-1}$. Although the deposition rate of BC in this study was not measured, we expect that the value could well be higher than those measured in European shelf sediments and dustfall from Beijing because of the large number of industrial plants in operation around Huangshi. The statistics showed that the consumption of coal in Huangshi in 2010 was 9.8 while that for petroleum was 0.38 million tons; these accounted for 61.47% and 4.88% of the total energy consumption in the city (http://www.hsfgw.gov.cn/xxgk/zfxxgkml/fzghjndjh/qsgmjshfzgh/201309/t20130915_157433.html). It is apparent that such a high consumption of fossil fuels could easily lead to the accumulation of high levels of BC in atmospheric dustfall.

It also has been shown that the stability of BC increases as the pyrolysis temperature increases (McBeath *et al.*, 2015), and this is relevant to our study because biomass burning derived BC is always produced at temperatures $< 400^\circ\text{C}$. This means that biomass-burning BC is dominated by labile or semi-labile compounds, both of which have relatively short half-lives. In comparison, BC produced from fossil fuel combustion always occurs at temperatures $> 600^\circ\text{C}$, and therefore fossil-fuel BC is mainly composed of stable compounds with comparatively long half-lives. In Huangshi, fossil fuel combustion was the main source for dustfall BC, and our data suggest that the BC in both soils and road dusts from the area is mainly from coal combustion. What's more, this pool of BC is likely to be highly resistant to mineralization, and therefore it has the potential to be preserved in the environment for centuries to millennia. Due to the extensive sorption of organic pollutants and toxic heavy elements onto BC (Cornelissen *et al.*, 2005; Lohmann *et al.*, 2005; Uchimiyama *et al.*, 2010), the distribution

of BC particles in dustfall could influence the mobility and bioavailability of these compounds, and these interactions could thus have important implications for human health.

CONCLUSIONS

This study provides basic information concerning the concentrations of BC, char, and soot in atmospheric dustfall from a typical industrial city in central China. The contents of BC, char, and soot at the different sampling sites showed high variability, suggesting heterogeneity among the emission sources. The spatial distributions of BC, char, and soot in atmospheric dustfall evidently were impacted by local emission sources; that is, high levels of BC were found adjacent to a thermal power plant and a railway line. Source identification studies based on BC/OC and char/soot ratios suggest that (1) BC mainly derives from fossil fuels, especially coal combustion, and (2) the contribution of BC from biomass burning is quite limited. However, in order to better understand the sources and residence time of these carbonaceous particles, stable isotopes of carbon and radiocarbon analysis will provide much valuable information, which requires further specific study of this phenomenon. Overall, the level of concentrations of carbonaceous particles in Huangshi are higher than those in some large cities and therefore potentially a serious health concern. Due to the high loadings of BC in dustfall, these findings highlight the need for attention from the local government as well as the importance of implementing effective measures to control carbonaceous pollution.

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