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Different characteristics of char and soot in the atmosphere and their ratio as an indicator for source identification in Xi'an, China

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Abstract

Elemental carbon (EC) is a collective term encompassing all thermally altered carbonaceous materials and can be subdivided into two classes: char and soot. Since the different classes of EC have different chemical and physical properties, their optical light-absorbing properties differ, so that it is essential to differentiate them in the environment. One year of observations of the daily and seasonal variations of carbonaceous particles were conducted in Xi'an, China in 2004 to demonstrate the different characteristics of char and soot in the atmosphere. Total carbon (TC), organic carbon (OC), EC and char-EC showed similar seasonal trends, with high concentrations in winter and low concentrations in summer, while soot-EC revealed relatively small seasonal variations, with maximum concentration (1.85 $\mu g\,m^{-3}$) in spring and minimum concentration (1.15 $\mu g\,m^{-3}$) in summer. The strong correlation between EC and char-EC (R^2=0.99) indicates that previously reported total EC reflected the characteristics of char only, while overlooking that of soot. However, soot exhibits stronger light-absorbing characteristics than char, and merits greater focus. The small seasonal variation of soot-EC indicates that soot may be the background fraction in total EC, and is likely to have an even longer lifetime in the atmosphere than previously estimated for total EC, which suggests that soot has a greater contribution to global warming. Although char-EC/soot-EC ratio is similar to primary OC/EC ratio as both vary with emission sources, OC/EC ratio is affected by the secondary organic aerosol (SOA) formation. Thus char-EC/soot-EC may be a more effective indicator than OC/EC in source identification of carbonaceous aerosol. Comparison of seasonal variations of OC/EC and char-EC/soot-EC ratios in Xi'an confirms this point. However, wet scavenging by snow and rain was more effective for char than for soot and influenced the char-EC/soot-EC ratio, and this factor should be considered in source identification as well.

1 Introduction

Previous studies of carbonaceous aerosols have focused on two main classes: organic carbon (OC) and elemental carbon (EC, also termed black carbon, BC). EC has received more attention in recent years because it contributes to global warming, carries carcinogenic compounds, and causes serious health risk (Jacobson, 2001; Menon et al., 2002; Avakian et al., 2002; Hansen and Nazarenko, 2004; Koelmans et al., 2006). It is estimated that the contributions by EC to global warming, in terms of direct climate forcing, is second only to CO_2 (Jacobson, 2001), and reducing emissions of EC could mitigate the projected warming trends and delay the time of onset of the "dangerous" climate change (e.g. Shindell and Faluvegi, 2009). Globally, biomass and biofuel burning contributes about 62% to total EC and fossil fuel about 38% (Bond et al., 2004). However, EC is not a single chemical compound with well-defined characteristics (Pöschl, 2005; Andreae and Gelencsér, 2006), but is best understood as a range of compounds occurring along a "combustion continuum" (Masiello, 2004; Koelmans et al., 2006). EC is generally subdivided into char and soot. Soot is composed of submicron particles formed from the condensation of hydrocarbon radicals at high temperature (>600°C). Char, unlike soot that forms submicron, grape-like clusters, retains the morphology of their source material with diameters ranging from 1 to 100 μm. Due to differences in the chemical and physical properties of char and soot (Masiello, 2004) and the resulting difference in optical light-absorbing properties (Kirchstetter et al., 2004; Reid et al., 2005; Andreae and Gelencsér, 2006), the differentiation between char and soot in the environment would help us better understand their environmental and climatic impacts.

There have been few studies discriminating between char and soot because the necessary methods have not been perfected. Recently, Han et al. (2007a) estimated to differentiate between char and soot using the thermal optical reflectance (TOR) method that has long been utilized in carbonaceous aerosol studies as the most reliable method (Gelencsér, 2004). Han et al. (2007a) found that char and soot evolved in different

conditions in the TOR method (char oxidized in EC1 conditions, at 550°C in a 2% O_2/98% He atmosphere, and soot in EC2 and EC3 conditions, at 700°C and 800°C in a 2% O_2/98% He atmosphere, respectively). Also, comparing the TOR method with the chemothermal (CTO-375) method indicated that soot-EC determined by the CTO-375 method (Nguyen et al., 2004; Hammes et al., 2007) always corresponded to EC2 and EC3 determined by the TOR method (Han et al., 2007b). This suggests that the TOR method can be used to operationally differentiate between char and soot (Han et al., 2007a).

In order to demonstrate the different characteristics of char and soot, one year of observations of the daily and seasonal variations of carbonaceous particles, including total carbon (TC), OC, EC, char-EC, and soot-EC in $PM_{2.5}$ (particulate matter with an aerodynamic diameter smaller than 2.5 micrometres [μm]) in Xi'an, China in 2004 are examined. In addition, as the primary particles of char and soot, their ratio is tested as means of source identification for carbonaceous aerosols. The influence of wet scavenging on the behavior of char and soot and their ratios is also discussed.

2 Sampling and analysis

2.1 Research area and sampling

Xi'an is the capital city of Shaanxi province in Central China, located on the Guanzhong Plain at 33°29′–34°44′ N, 107°40′–109°49′ E (Fig. 1). The city is situated in a semi-arid zone, with a mean temperature of 13.0–13.4°C and annual rainfall of 558–750 mm. Rainfall generally occurs during July and September due to the East Asian monsoon system.

Sampling was carried out on the rooftop of the building of the Institute of Earth Environment, Chinese Academy of Sciences, at 10 m above ground, which is surrounded by a residential area ~15 km south of downtown (Fig. 1) and has no major industrial activities. Daily $PM_{2.5}$ samples were collected from 1 January to 31 December

using mini-volume samplers (Airmetrics, Oregon, USA) operating at flow rates of 5 L per minute (L min^{-1}). All samples were acquired on pre-fired (900°C for three hours), pre-weighed 47 mm Whatman quartz-fiber filters for 24 h from 10:00 a.m. to 10:00 a.m. every day.

Meteorological data were monitored simultaneously with a HFY-IA Wind Speed/Wind Direction Instrument (Changchun Institute of Metrological Instruments, Changchun, Jilin Province, China). Meanwhile, daily temperatures and weather conditions such as rain, snow, dust storms, and visibility issued by the Xi'an Meteorological Bureau were manually recorded. Based on local meteorological characteristics, the four seasons were designated as January, February and December for winter, March to May for spring, June to August for summer, and September to November for fall.

2.2 Carbon analysis

Samples were analyzed gravimetrically for mass concentrations using an electronic microbalance with ±1 μg sensitivity (Sartorius, Gottingen, Germany). Carbon analyses were conducted with a Desert Research Institute (DRI) Model 2001 Carbon Analyzer (Atmoslytic Inc., Calabasas, CA) following the IMPROVE TOR protocol (Chow et al., 1993; Han et al., 2007a, b). A 0.526 cm^2 punch from a quartz filter was heated to produce four OC fractions: OC1, OC2, OC3, and OC4 at temperatures of 120, 250, 450, and 550°C, respectively, in a non-oxidizing helium (He) atmosphere, and three EC fractions: EC1, EC2, EC3 at 550, 700, and 800°C, respectively, in an oxidizing atmosphere of 2% oxygen/98% helium. Meanwhile, a pyrolyzed organic carbon fraction (POC) was also produced and was determined when a reflected laser light attained its original value after O_2 was added to the analysis atmosphere. IMPROVE OC is defined as the sum of the four OC fractions plus POC, and EC as the sum of the three EC fractions minus POC. The sum of OC and EC is total carbon (TC). According to Han et al. (2007a), char-EC is defined as EC1 minus POC, and soot-EC as the sum of EC2 and EC3. This differentiation has been used in both aerosol (Han et al., 2008) and sediment studies (Han et al., 2009a), as well as in soils and urban dusts to indicate

local air pollution problems in China (Han et al., 2009b).

The analyzer was calibrated with known quantities of CH_4 every day. Average concentrations of filter blanks were 1.56, 0.42, 0.32, and 0.10 $\mu g\,m^{-3}$ for OC, EC, char-EC, and soot-EC, respectively, which were subtracted from the ambient measurements. Replicate analyses were performed at the rate of one per group of 10 samples. Comparison with average values from replicate analyses showed errors were <5% for TC, <8% for OC and EC, and <10% for char-EC and soot-EC.

3 Results

Daily and monthly variations in OC, EC, char-EC, and soot-EC, as well as daily mass and TC variations are shown in Figs. 2 and 3. Also, seasonal mass and carbon concentrations are summarized in Table 1. The annual average $PM_{2.5}$ mass concentration was 178.5 $\mu g\,m^{-3}$, which is much higher than the National Ambient Air Quality Guideline of the European Union (25 $\mu g\,m^{-3}$), as well as the Air Quality Guideline and the Interim Target-3, -2 and -1 of the World Health Organization (WHO) of 10, 15, 35, 35 $\mu g\,m^{-3}$, respectively, indicating a very serious potential health concern for local residents. Average OC and EC concentrations were 36.39 and 8.41 $\mu g\,m^{-3}$, respectively, contributing to 20.4% and 4.7% of the total $PM_{2.5}$ mass, respectively. Comparing EC concentrations in Xi'an with those of other Chinese cities reported in previous studies (e.g. He et al., 2001; Cao et al., 2003, 2007; Ye et al., 2003; Yu et al., 2004; Duan et al., 2007) indicated EC rank highly in Xi'an, and this may also imply that char-EC rank highly since char-EC are well correlated with EC in different Chinese cities (Han et al., 2009). This finding is consistent with a previous study on the spatial distribution of EC and char-EC from 14 Chinese cities (Cao et al., 2007; Han et al., 2009). Average char-EC and soot-EC concentrations were 6.86 and 1.54 $\mu g\,m^{-3}$, accounting for 81.6% and 18.4% of the total EC, respectively. The char-EC level was about 6 times higher than that in a small village in Daihai, Inner Mongolia (Han et al., 2008), which can be attributed to the difference in fuel consumption between Xi'an, a mega-city, and

Daihai, a rural mountain area. The average soot-EC concentration in Xi'an was close to the average soot-EC concentration (1.24 $\mu g\,m^{-3}$) from 14 Chinese cities (Han et al., 2009), which confirms the very small difference in soot-EC concentrations at large.

4 Discussion

4.1 Variations in char-EC and soot-EC concentrations

Concentrations of $PM_{2.5}$, TC, OC, EC, and char-EC showed similar patterns, with high concentrations in winter and low concentrations in summer. This pattern is similar to previous studies (e.g. Cao et al., 2003, 2005, 2007; Han et al., 2008) and is consistent with fuel consumption as winter heating generates heavy emissions in Xi'an (Han et al., 2009). Soot-EC concentrations revealed a slightly different pattern, with the highest monthly concentrations in spring (March and April), but the lowest soot-EC level still occurred in summer. This trend is similar to that found in a previous study in a remote mountain area of Inner Mongolia in northern China (Han et al., 2008), and is similar with CO variation with maximum concentration occurring during local spring in both Northern and Southern Hemispheres (Yung et al., 1999). Both soot and CO come mainly from fossil fuel combustion and biomass burning. In China, forest fires frequently occur in spring (March and April) after the long-term dry season in winter, which may contribute to the high soot-EC concentrations at that time. Comparison of daily, monthly and seasonal variations of char-EC and soot-EC concentrations (Fig. 3) indicated that abundance of char-EC was more variable. The maximum and minimum seasonal average char-EC concentrations were 10.49 and 2.57 $\mu g\,m^{-3}$, respectively. Soot-EC showed a narrower seasonal variation, with a maximum level in spring (1.85 $\mu g\,m^{-3}$) and minimum level in summer (1.15 $\mu g\,m^{-3}$). If the influence of wet scavenging (see Sect. 4.4) is neglected, the seasonal variations in soot-EC concentrations may be even smaller, and this implies that soot may have an even longer lifetime than previously estimated for total EC (Orgen and Charlson, 1983).

4.2 Correlations between different carbon particles

Correlations between different carbonaceous materials are presented in Table 2. Similarly to many previous studies (e.g. Cao et al., 2003, 2005; Duan et al., 2007; Han et al., 2008), OC and EC in Xi'an were positively correlated ($p<0.0001$), indicating common combustion sources for carbonaceous aerosols in urban areas. Char-EC showed stronger correlation with TC, OC, and EC than soot-EC, which may be a result of the different formation mechanism of char and soot (Han et al., 2009b), with char formed from combustion residues and soot from gas-particle re-condensation. EC had the strongest correlation with char-EC among these components, which is consistent with char-EC dominating the total EC. The regression equation between EC and char-EC (Fig. 4) is EC=1.15+1.06*char-EC (R^2=0.99). The slope and intercept are similar to those obtained from the correlations between EC and char-EC from fourteen Chinese cities (Han et al., 2009). This further confirms that previously reported EC concentrations measured with the TOR method can be used to calculate char-EC concentrations in urban areas. Since EC is the sum of char-EC and soot-EC, the intercept of 1.15 $\mu g\,m^{-3}$ can be seen as the background value of soot-EC in Xi'an. This value is similar to the average concentration of soot-EC in summer. In the different seasons throughout the year, motor vehicle activities vary little, while coal heating is concentrated in winter, so the background of soot may be derived mainly from vehicle exhaust. Previous researchers have referred to EC as a "proxy" for the concentration of soot carbon (see review by Andreae and Gelencsér, 2006). Our results suggest that previously reported EC may reflect char variations only.

EC and char-EC are moderately correlated with soot-EC in Xi'an, which may be affected by the background value of soot-EC. However, this relationship is stronger than that from fourteen Chinese cities (Han et al., 2009), which showed poor correlation between char-EC and soot-EC. This result may be associated with the relatively limited sources for EC emissions in Xi'an compared with those from the fourteen cities, which is shown by the narrow range of char-EC/soot-EC ratios from primary Xi'an coal com-

bustion emissions (1.5–3.0 from Cao et al. (2005) vs. 1.2–66.7 from Fig. 6). Comparison of the correlations between char-EC and soot-EC among the different four seasons (Fig. 5) showed increasing slopes and correlations from winter to summer, consistent with the increasing contribution of soot-EC to total EC with the enhanced percentage of motor vehicle emissions in summer.

4.3 Char-EC/soot-EC ratio as an indicator for source identification

4.3.1 Char-EC/soot-EC ratios from primary emissions

EC forms from all combustion processes with three main sources: biomass burning, coal combustion, and motor vehicle exhaust. It has been suggested that primary emissions have distinct OC/EC ratios, with higher values from biomass burning and lower levels from fossil fuel combustion (e.g. Turpin and Huntzicker, 1991; Castro et al., 1999; Cao et al., 2003, 2005, 2007; Malm et al., 2004; Zhang et al., 2007). Similarly, char-EC/soot-EC ratios also have distinct values from primary emissions (Chow et al., 2004; Cao et al., 2005, 2006; Han et al., 2008). Ambient OC/EC ratio is generally influenced by three factors: primary emission source, different OC and EC removal rates by deposition, and secondary organic aerosol (SOA) formation (Cachier et al., 1996; Cao et al., 2005). However char-EC/soot-EC ratio is controlled predominately by combustion process and remains stable in the environment, and thus is determined only by the first two factors. Since SOA accounts for a substantial fraction of carbon in aerosol (Turpin and Huntzicker, 1991; Castro et al., 1999; Cao et al., 2003; Schichtel et al., 2008) and it is not easy to obtain the exact percentage (Turpin and Huntzicker, 1991; Castro et al., 1999), substantial bias may exist in source identification using the OC/EC ratio. This problem does not exist for the char-EC/soot-EC ratio, and thus it may be better to use the char-EC/soot-EC ratio for source identification.

Primary emissions of OC/EC and char-EC/soot-EC ratios from biomass burning, coal combustion, vehicle exhaust, and cooking are presented in Fig. 6. Since there are few reports of char-EC and soot-EC from primary emissions, OC/EC and char-EC/soot-EC

ratios in Fig. 6 are calculated using the raw data reported from the eight carbon fractions in the literature measured with the TOR method (Chow et al., 2004; Cao et al., 2005, 2006; Chen et al., 2007; and some unpublished data from Yuan Liu). Details for the combustion conditions can be found in these articles. Motor vehicle emissions have the lowest OC/EC and char-EC/soot-EC ratios, with char-EC/soot-EC generally lower than 1.0. Coal combustion and biomass burning have higher, albeit distinct, OC/EC and char-EC/soot-EC ratios, which may be controlled mainly by the fuel types, combustion mode and temperature, and moisture content, etc. The ratios depend on the mixing function of the different factors. For example, grass combustion may produce lower char-EC/soot-EC, while wood combustion has higher char-EC/soot-EC (Chow et al., 2004; Chen et al., 2007). Generally, biomass burning by smoldering at low temperatures results in high char-EC/soot-EC (Chen et al., 2007). In coal combustion, bituminous coal generally produces very high char-EC/soot-EC, while anthracite coal produces relatively lower char-EC/soot-EC. Residential coal combustion in Xi'an has char-EC/soot-EC ranging from 1.5 to 3.0 (Cao et al., 2005). Residential cooking produces char-EC/soot-EC generally within the range of 2.0 to 6.0 (Chow et al., 2004).

4.3.2 Source identification from char-EC/soot-EC ratios in Xi'an

Daily variations in OC/EC and char-EC/soot-EC ratios are presented in Fig. 7. The average OC/EC ratios in winter and summer have almost similar values, and the lowest ratios occurred in spring (Table 1). Monthly variations in OC/EC ratios revealed two peaks, in January and July, respectively (Fig. 3). The first peak can be ascribed to the coal consumption in winter, although SOA formation may also have an important impact (Cao et al., 2005). The next peak is most likely to be linked to SOA formation since motor vehicle exhaust are the main contributor to EC in summer, which have very low primary OC/EC ratios (Fig. 6), and the higher temperature in summer would produce more SOA (e.g. Turpin and Huntzicker, 1991). This confirms that OC/EC ratio is not universally suitable for primary source identification of carbonaceous aerosols, since it is not only influenced by the fuel used (the primary emissions), but also by the

formation of SOA.

Unlike OC/EC, char-EC/soot-EC ratios showed a clear seasonal variation, with the highest value of 6.69 in winter and the lowest value of 2.17 in summer. Xi'an has a long-term "heating season" from October 15 to March 15 (Cao et al., 2005). It was reported (Xi'an Clean Energy Office, 2002) that 3.5 Tg coal was consumed as the main energy source in the total primary energy consumption in 2000, which accounts for 81% of the total energy consumption. Obviously, the high char-EC/soot-EC ratios in winter can be attributed to coal consumption for heating. The average char-EC/soot-EC ratio in summer was still higher than that from road dusts (1.66) in Xi'an city (Han et al., 2009b), which may suggest that apart from the main contributions from motor vehicle exhaust, industrial coal combustion and some biomass burning events in summer cannot be neglected in summer. For example, the biomass burning occurred during June 8 and 9 in rural area around Xi'an caused a sharp increase in char-EC/soot-EC ratio, with values close to 10 (Fig. 6). Monthly char-EC/soot-EC ratios showed their highest peak in February (Fig. 3), with a small decreasing trend in January and December, probably due to the difference in wet scavenging rates by snow and rain between char and soot particles (see Sect. 4.4). Obviously, the variations in char-EC/soot-EC ratio are consistent with the energy sources and thus are effective indicator for source identification. Since char-EC/soot-EC is well correlated with char-EC concentrations (Table 2), char-EC variation may be roughly used for source identification of carbonaceous aerosols.

4.4 Wet scavenging influencing the discrepancy in char and soot removal

Generally, carbon concentrations in urban areas are mainly determined by the fuel consumption. TC, OC and EC, as well as char-EC (Figs. 2 and 3), showed high concentrations in winter and low concentrations in summer, which is in good agreement with fuel consumption in Xi'an. Although temperature itself should not affect carbon concentrations, it is negatively correlated with the mass and carbon concentrations (Table 2). Temperature varies with coal combustion, as well as mixing height in Xi'an, which would influence carbon concentrations. For example, in winter, especially in cold

weather, more coal is used for heating in Xi'an, which would result in higher emissions. Meanwhile low temperatures would lead to a lower mixing height, reducing particulate dispersion and thus enhancing local pollutant levels. The daily minimum temperature showed relatively stronger correlations with carbon concentrations and char-EC/soot-EC ratio than the daily maximum temperature, which may be attributed to increased coal combustion during cold periods.

Rain and snow were thought to be important factors influencing atmospheric aerosol concentrations due to their scavenging potential (e.g. Armails, 1999; Jaffe et al., 2005; Meng et al., 2007). Generally, high precipitation occurs in summer and lower precipitation in spring and winter in northern China, including Xi'an, due to the influence of the East Asian monsoon system (Han et al., 2009c). Although the lowest precipitation occurs in spring in Xi'an, the highest concentrations of mass, TC, OC, EC, and char-EC occurred in winter, but not in spring, which may suggest that, for these components, the influence of fuel consumption is more important than wet scavenging. Soot-EC concentrations showed close coupling with the snow and rain precipitation, with the highest in spring (March and April), and the lowest in summer (Figs. 2, 3, and 7). This pattern may suggest that soot, as a regionally-to-globally dispersed particle, is affected mainly by wet precipitation.

The comparison of seasonal variations between rainy and non-rainy period (Table 3) indicates that rain removal is more effective in dry season (winter and spring) than in wet season (summer and fall) for TC, OC, EC, char-EC and soot-EC. This finding is similar to that of Armails (1999), who found that the wet deposition of EC was double during the dry season than during the wet season. Generally, in winter the high pressure associated with the invasion of cold air prevents the air mass diffusion, so that snow or rain precipitation is the main route for EC removal. In summer, the low pressure and higher mixing height facilitates EC diffusion and thus rain precipitation would be a relatively less effective factor influencing pollutant removal. The char-EC/soot-EC ratio variations were also affected by wet precipitation, and showed a great decrease in rainy periods (Table 3). This suggests that char and soot have different removal rates

by wet scavenging, which may be mainly associated with the difference in char and soot particle sizes. In general, char is composed of large particles (1–100 μm) produced from incomplete combustion at low temperatures, and would be expected to be easily been removed by wet deposition. Soot, composed of submicron particles, can remain suspended for time scales of the order of a month (Ogren and Charlson, 1983), and thus is more difficult to remove.

5 Conclusions

This study demonstrates that char and soot have different characteristics in the atmosphere. Similar to previous reported TC, OC and total EC, char-EC showed high seasonal variations, with the maximum concentrations in winter (10.49 $\mu g\,m^{-3}$) being ~4 times of that in summer (2.57 $\mu g\,m^{-3}$). This is associated with Xi'an winter heating. However, soot-EC revealed only small variations in different seasons, highest in spring and lowest in summer, and this variation is probably in part due to the wet scavenging. This confirms the regional-to-global dispersion of soot particles, while char is relatively locally to regionally distributed. Strong correlations between EC and char-EC suggest that char-EC concentrations can be calculated from previously reported EC concentrations. However, previously reported total EC in the literature reflected the characteristics of char only, while soot's characteristics were overlooked. Soot-EC can be seen as a background fraction, contributing to 18.4% of Xi'an total EC on average, and had a background value of ~1.15 $\mu g\,m^{-3}$ in $PM_{2.5}$, which may be mainly associated with the motor vehicle emission throughout the year. Previous studies suggested that soot exhibits strong light absorption characteristics with little spectral dependence; while char tends to absorb strongly in the UV spectrum. Thus, efforts to reduce motor vehicle emissions may have a greater impact on the mitigation of the present warming trends than the reduction of biomass burning and coal combustion. The primary emissions had the lowest char-EC/soot-EC ratios from motor vehicle exhaust (less than 1.0 in general), while high values were generated by coal combustion and biomass burning (up to ~70). This indicates that char-EC/soot-EC ratio is an effective indicator of source identification for carbonaceous aerosols. However, wet scavenging is also an important factor influencing the char-EC/soot-EC ratio because of the difference in removal rate of char and soot. The seasonal char-EC/soot-EC ratios in the rainy period are much lower than those in non-rainy period, which is consistent with the physical properties of char and soot, in particular their size distributions. Since a limited amount of data is now available concerning source emissions of OC/EC and char-EC/soot-EC ratios, more studies in different source emissions are needed in the future. In addition, such studies may help to establish the relationship between primary OC/EC and char-EC/soot-EC ratios, providing new insights on methods for SOA calculation.

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Table 1. Seasonal variations of mass, total carbon (TC), organic carbon (OC), elemental carbon (EC), OC/EC, char-EC, soot-EC, and char-EC/soot-EC.

Seasons	Concentrations	Mass $\mu g\,m^{-3}$	TC $\mu g\,m^{-3}$	OC $\mu g\,m^{-3}$	EC $\mu g\,m^{-3}$	OC/EC	Char-EC $\mu g\,m^{-3}$	Soot-EC $\mu g\,m^{-3}$	Char-EC/soot-EC
Winter	Min	59.20	14.52	10.45	3.56	2.56	2.39	0.62	1.37
(*n*=90)	Max	651.26	217.00	192.66	29.09	9.72	26.95	3.08	14.71
	Average	235.41	74.05	61.96	12.08	5.35	10.49	1.60	6.69
	SD[a]	125.14	40.01	34.94	6.22	1.71	5.95	0.54	3.31
Spring	Min	28.40	4.66	4.18	0.42	2.04	0.19	0.23	1.08
(*n*=87)	Max	404.48	120.35	98.87	21.48	9.89	19.58	4.61	18.92
	Average	152.14	38.04	28.67	9.37	3.27	7.52	1.85	4.14
	SD	72.76	20.48	16.10	4.86	1.11	4.44	0.72	2.61
Summer	Min	29.23	6.26	5.67	0.51	1.92	0.20	0.28	0.63
(*n*=89)	Max	217.30	56.68	46.20	11.07	11.67	9.88	2.24	8.82
	Average	105.49	19.58	15.86	3.72	5.13	2.57	1.15	2.17
	SD	38.34	8.41	6.71	2.13	2.31	1.82	0.47	1.30
Fall	Min	28.94	5.43	4.47	0.97	2.61	0.66	0.29	0.57
(*n*=88)	Max	627.14	145.27	123.47	22.85	8.79	19.81	3.60	20.77
	Average	179.70	47.05	38.62	8.43	4.62	6.85	1.58	4.62
	SD	115.56	30.17	25.80	4.79	1.21	4.60	0.59	3.62
Whole year	Average	178.54	44.79	36.39	8.41	4.61	6.86	1.54	4.41
	SD	113.83	33.75	28.90	5.61	1.84	5.28	0.64	3.27

[a] SD is standard deviation.

Table 2. Correlations among total carbon (TC), organic carbon (OC), elemental carbon (EC), OC/EC, char-EC, soot-EC, and char-EC/soot-EC, as well as high and low temperatures.

	TC	OC	EC	OC/EC	Char-EC	Soot-EC	char-EC/soot-EC	Low Temp.	High Temp.
TC		0.996	0.885	0.148	0.9	0.335	0.8	−0.62	−0.561
OC	0.000		0.839	0.217	0.858	0.282	0.782	−0.615	−0.567
EC	0.000	0.000		−0.226	0.995	0.561	0.78	−0.559	−0.456
OC/EC	0.005	0.000	0.000		−0.178	−0.517	0.011	−0.082	−0.157
Char-EC	0.000	0.000	0.000	0.001		0.476	0.826	−0.562	−0.46
Soot-EC	0.000	0.000	0.000	0.000	0.000		0.025	−0.269	−0.208
char-EC/soot-EC	0.000	0.000	0.000	0.844	0.000	0.645		−0.544	−0.454
Low Temp.	0.000	0.000	0.000	0.122	0.000	0.000	0.000		0.952
High Temp.	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.000	

The right upper part is correlation coefficient; the left lower part is significant level.

Table 3. Comparison of different seasonal $PM_{2.5}$ mass, total carbon (TC), organic carbon (OC), elemental carbon (EC), char-EC, and soot-EC concentrations, as well as OC/EC, char-EC/soot-EC between rainy and non-rainy periods. Any day with rain is classified into rainy period. Snow days are also included into rainy period.

Seasons	Condition	Mass $\mu g\,m^{-3}$	TC $\mu g\,m^{-3}$	OC $\mu g\,m^{-3}$	EC $\mu g\,m^{-3}$	OC/EC	Char-EC $\mu g\,m^{-3}$	Soot-EC $\mu g\,m^{-3}$	Char-EC/ Soot-EC	N[b]
Winter	Non-rain	240.08	79.60	66.49	13.11	5.28	11.47	1.64	7.21	77
	Rain	207.73	41.16	35.15	6.01	5.77	4.67	1.34	3.59	13
	Ratio[a]	1.16	1.93	1.89	2.18	0.92	2.46	1.23	2.01	
Spring	Non-rain	158.63	39.87	30.04	9.84	3.18	7.95	1.88	4.36	78
	Rain	95.88	22.11	16.83	5.28	4.08	3.73	1.55	2.29	9
	Ratio	1.65	1.80	1.78	1.86	0.78	2.13	1.22	1.90	
Summer	Non-rain	106.63	20.35	16.42	3.93	5.01	2.75	1.18	2.24	71
	Rain	101.00	16.52	13.65	2.87	5.58	1.83	1.03	1.90	18
	Ratio	1.06	1.23	1.20	1.37	0.90	1.50	1.14	1.18	
Fall	Non-rain	190.36	52.14	42.72	9.42	4.48	7.80	1.62	5.27	67
	Rain	145.69	30.82	25.55	5.28	5.08	3.83	1.45	2.54	21
	Ratio	1.31	1.69	1.67	1.78	0.88	2.04	1.12	2.08	

[a] Ratio is that of non-rain to rain data;
[b] N is sample number.

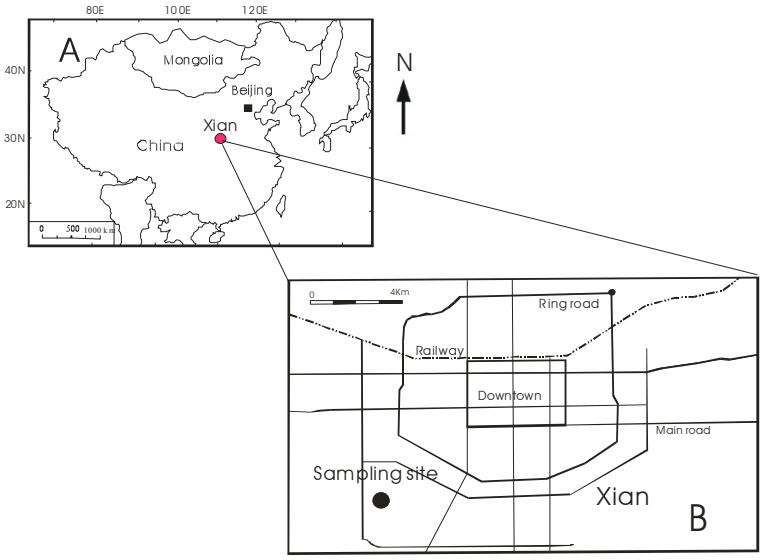

Fig. 1. Sampling site at Xi'an, Central China.

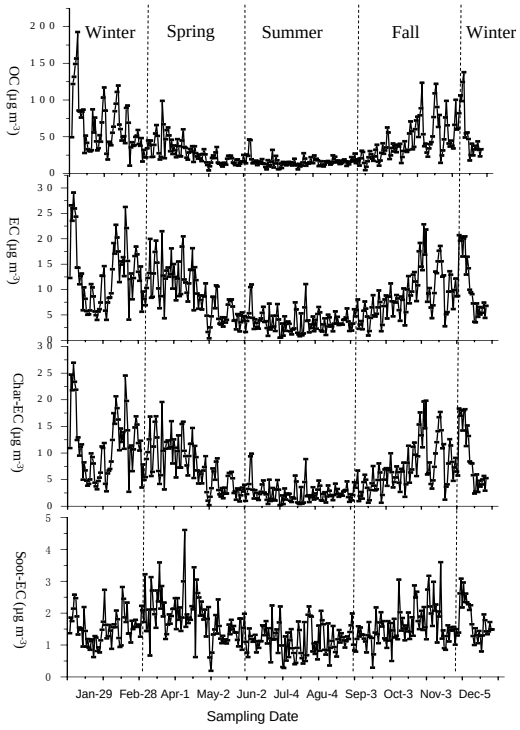

Fig. 2. Daily variations of organic carbon (OC), elemental carbon (EC), char-EC, and soot-EC concentrations in Xi'an in 2004.

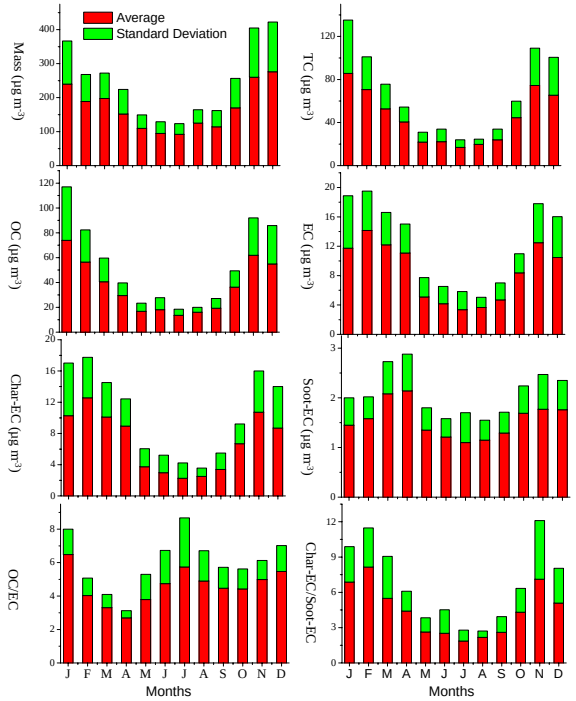

Fig. 3. Monthly variations of mass, total carbon (TC), organic carbon (OC), elemental carbon (EC), char-EC, and soot-EC concentrations, as well as OC/EC and char-EC/soot-EC ratios in Xi'an in 2004.

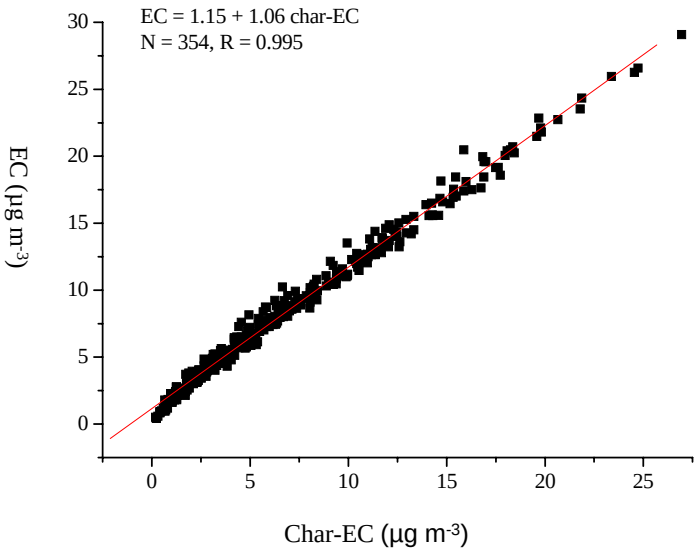

Fig. 4. Strong correlation between elemental carbon (EC) and char-EC.

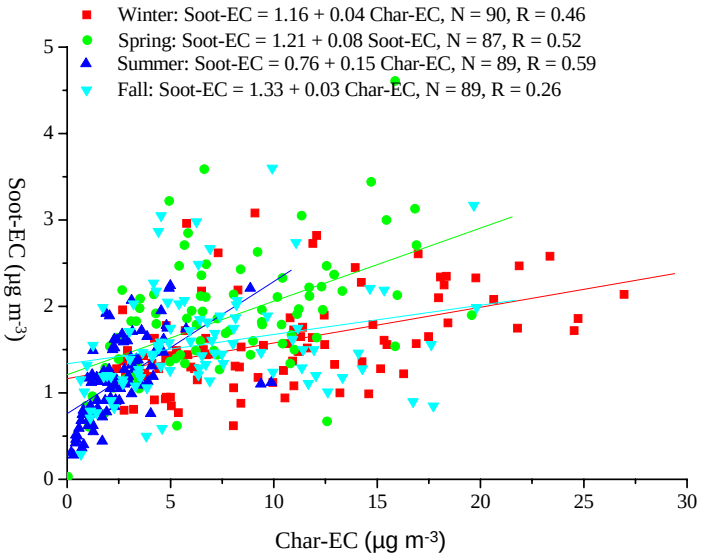

Fig. 5. Comparison of correlations between char-EC and soot-EC in different seasons in 2004.

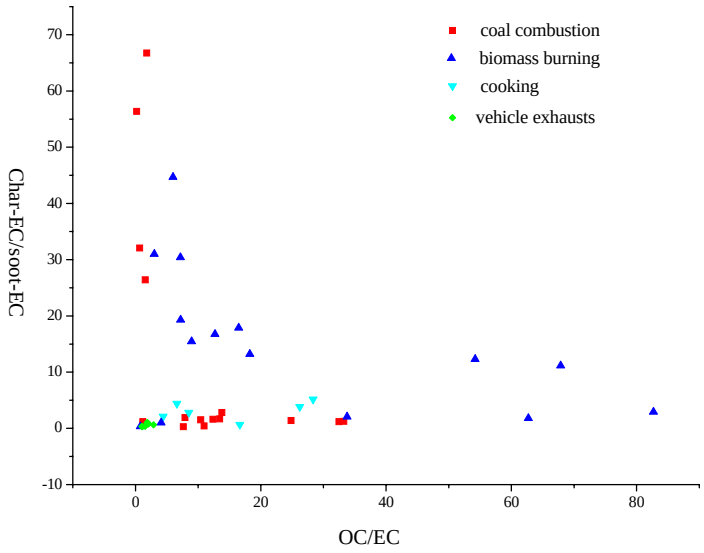

Fig. 6. Picture of the primary emissions of OC/EC ratios and char-EC/soot-EC ratios from different sources. Yuan Liu in the Department of Environmental Science and Engineering, Beijing University of China provides some unpublished data, with sampling following Liu et al. (2007). Motor vehicle samples are from Cao et al. (2006) and Chow et al. (2004) using a ground-based source-dominated sampling method; meat cooking samples from Chow et al. (2004) using an exhaust dilution method; coal samples from Chen et al. (2007), Chow et al. (2004) and Liu (2007) using an exhaust dilution method and from Cao et al. (2005) using a ground-based source-dominated sampling method; biomass burning samples from Chow et al. (2004) and Cao et al. (2005) using a ground-based source-dominated sampling method and from Chen et al. (2007) and Liu et al. (2007) using an exhaust dilution method.

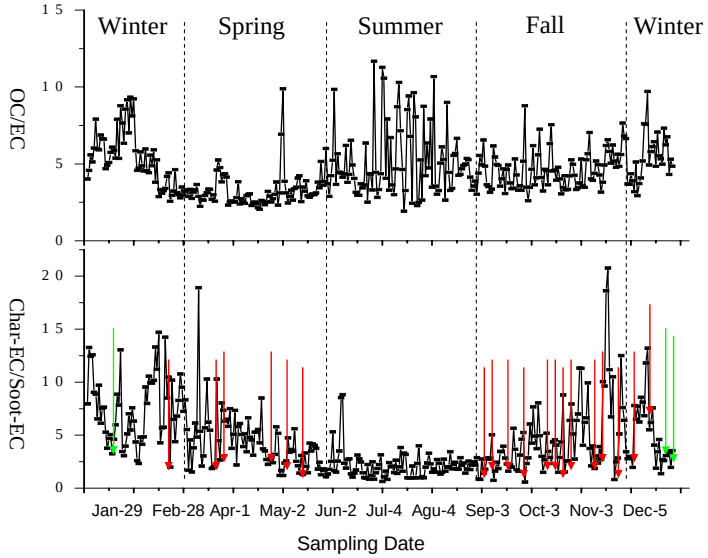

Fig. 7. Temporal variations of OC/EC and char-EC/soot-EC, as well as the relation between char-EC/soot-EC and rain and snow in 2004. Red and green arrows represent rain and snow days, respectively, and the arrow locations correspond to the char-EC/soot-EC ratio. Note that not all the rainy and snow days are present, with some continuous days are showed with one arrow. Rainy days in summer are not presented since there are only small variations of char-EC/soot-EC between rainy and non-rainy days.