



## Comparison and implications of PM<sub>2.5</sub> carbon fractions in different environments



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### HIGHLIGHTS

- The eight carbon fractions, char and soot at rural, urban, tunnel and remote sites were compared.
- OC/EC and char/soot among four sites were elucidated as effective source indicator.
- The results might give implications for models in estimating their climate effects.

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### ABSTRACT

The concentrations of PM<sub>2.5</sub> carbon fractions in rural, urban, tunnel and remote environments were measured using the IMPROVE thermal optical reflectance (TOR) method. The highest OC1 and EC1 concentrations were found for tunnel samples, while the highest OC2, OC3, and OC4 concentrations were observed for urban winter samples, respectively. The lowest levels of most carbon fractions were found for remote samples. The percentage contributions of carbon fractions to total carbon (TC) were characterized by one peak (at rural and remote sites) and two peaks (at urban and tunnel sites) with different carbon fractions, respectively. The abundance of char in tunnel and urban environments was observed, which might partly be due to traffic-related tire-wear. Various percentages of optically scattering OC and absorbing EC fractions to TC were found in the four different environments. In addition, the contribution of heating carbon fractions (char and soot) indicated various warming effects per unit mass of TC. The ratios of OC/EC and char/soot at the sites were shown to be source indicators. The investigation of carbon fractions at different sites may provide some information for improving model parameters in estimating their radiative effects.

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### 1. Introduction

Carbonaceous aerosols, including organic carbon (OC) and elemental carbon (EC), are ubiquitous species in the atmosphere and exert an important influence on environments, health and climate systems (Poschl, 2005; Jacobson, 2006; Schmidl et al., 2008; Schwarz et al., 2008; Cao et al., 2009; Feng et al., 2009; Satsangi et al., 2012). OC is derived from both primary sources (e.g., fossil fuel combustion and biomass burning) and secondary sources, whereas EC is exclusively

derived from primary sources. At present, the analysis of carbonaceous fractions is carried out by determining the bulk content of OC and EC, including OC1–4, OP, EC1–3, POC, SOC, char and soot. The analysis of individual substances in single fractions at the molecular level is still challenging (Grabowsky et al., 2011).

The distribution of carbon fractions varies spatio-temporally, which largely contributes to the physical and chemical characteristics of carbonaceous aerosols (Cao et al., 2005, 2007; Wang et al., 2006; Shen et al., 2007; Zhang et al., 2008, 2009; Zhu et al., 2010). The potential modification of climate systems by carbonaceous aerosols has been reported previously (Jacobson, 2006). The conclusions from this study suggested that enhanced global warming may partly result from the effect of EC in the atmosphere. Furthermore, when considering the cooling effect of OC, carbonaceous aerosols with a lower OC/EC ratio generally have a greater warming effect per unit mass of TC than those with higher ratios (Cao et al., 2007). Previous

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studies have also reported that the OC/EC ratios of carbonaceous aerosols vary largely due to different sources and aging evolution. These results indicated that the estimation of the radiative effects of carbonaceous aerosols using models is complicated (Kopp and Mauzerall, 2010). Large variations were observed when the importance of carbonaceous aerosols as global warming agents was estimated using models, which was mainly due to the inclusion or exclusion of certain physical effects of the carbonaceous particles (Jacobson, 2006; Forster et al., 2007). Therefore, it is essential to investigate the eight carbon fraction profiles and the ratios of OC/EC and char/soot in various environments.

In order to determine the levels of carbon fractions at various sites, measurements and comparisons of these species (including OC1–4, OP, EC1–3, POC, SOC, char and soot) in rural, urban, tunnel and remote environments were conducted. The characteristics of the carbon fractions were evaluated at the sites with different sources and aging evolution processes. This is the first study to compare the ratios of OC/EC and char/soot at four different sites, which will provide further information on the use of these ratios as effective indicators. These results may also provide data on the use of models to assess the properties of the carbon fractions in estimating their effects on climate.

## 2. Materials and methods

### 2.1. Sample collection

The PM<sub>2.5</sub> samples were collected at rural, urban, tunnel and remote sites, respectively. The urban sampling site was located at Xi'an, China (an urban-scale site on the rooftop of the Institute of Earth Environment, Chinese Academy of Sciences) (Cao et al., 2005). The rural site was in the typical rural area of Shaanxi, China, including three sites in Lintong, Huxian and Weinan county, respectively. In the research area it was common for residents to use straw and corn stake burning for cooking and heating in winter. The frequency of cooking was three times daily during the sampling period (Zhu et al., 2012a, b). The remote sampling site was at Qinghai Lake (a sampling tower at the "Bird Island" peninsula), in the Northeastern Qinghai–Tibet Plateau and the tunnel samples were collected at Hsuehshan Tunnel in Taiwan (Chen et al., 2010). Mini-Vol samplers (Airmetrics, USA) were used to collect the samples in both the rural and urban sites, each sampling lasted for 24 h operating at a flow rate of 5 L min<sup>-1</sup>. All samples were collected on 47 mm Whatman quartz microfibre filters (QM/A). A Tisch (TE-6001 Hi-vol PM<sub>2.5</sub> sampler) with the flow rate of 1000 L min<sup>-1</sup> and Dichotomous samplers with the value of 16.7 L min<sup>-1</sup> (Model SA-241, Andersen Inc., Georgia, USA) were used to collect PM<sub>2.5</sub> samples at the remote and tunnel sites, respectively. These samplers were all popularly used and the sampling artifacts were also discussed in the previous study (Zhu et al., 2012a,b). All quartz filters were pre-heated at 900 °C for 3 h and then stored in aluminum foil before sampling. The filters were stored in a refrigerator after sampling to prevent the evaporation of volatile components. The samples for rural and urban sites were collected in winter (December, 2007) and summer (June, 2008), respectively. Sampling campaign was conducted to collect 25 samples at the remote site. The detailed sampling procedure for the tunnel site (9 campaigns) was described elsewhere (Chen et al., 2010). Certainly, there are also some limitations in the study, including different samplers using, sampling artifacts and the uncertainty of the thermal optical analysis.

### 2.2. Carbonaceous aerosol measurement

All the PM<sub>2.5</sub> filters were analyzed for carbon fractions using a DRI Model 2001 thermal/optical carbon analyzer (Atmoslytic Inc., Calabasas, CA, USA). Using a punch from the quartz filter, three EC fractions and four OC fractions were analyzed following the IMPROVE-A (Interagency Monitoring of Protected Visual Environments) thermal/optical reflectance (TOR) protocol (Chow et al., 2007). The method produced data for

four OC fractions (OC1, OC2, OC3, and OC4 in a helium atmosphere at 140 °C, 280 °C, 480 °C, 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 2% oxygen/98% helium atmosphere at 580 °C, 740 °C, and 840 °C, respectively). The IMPROVE protocol defined OC as OC1 + OC2 + OC3 + OC4 + OP and EC as EC1 + EC2 + EC3 – OP. The EC fraction was also divided into char and soot. Char is defined as EC1 minus OP, and soot is defined as the sum of EC2 and EC3 (Han et al., 2009). The detailed quality assurance/quality control (QA/QC) procedures are described elsewhere (Chow et al., 2011). The analyzer was calibrated with known quantities of CH<sub>4</sub> each day. Replicate analyses were performed once every ten samples. A blank sample was also analyzed in order to correct the sample results.

## 3. Results and discussion

### 3.1. Characteristics of the eight carbon fractions from various environments

Table 1 shows the concentrations of carbon fractions for rural, urban, tunnel and remote samples. The levels of OC1–4 varied widely at the various sites. The average concentration of OC1 was highest in the tunnel (10.22 μg m<sup>-3</sup>). Average OC1 concentrations for rural winter (6.79 μg m<sup>-3</sup>) and urban winter (6.19 μg m<sup>-3</sup>) samples were higher than those for rural summer (0.79 μg m<sup>-3</sup>) and urban summer (2.64 μg m<sup>-3</sup>) samples, respectively. Comparable levels of OC2 were found in the rural winter (9.93 μg m<sup>-3</sup>), urban winter (10.12 μg m<sup>-3</sup>) and tunnel environments (8.35 μg m<sup>-3</sup>). OC2 also showed distinctive seasonal variation with higher values in winter than in summer for rural and urban sites, respectively. Average OC3 of rural and urban samples was 10.84 and 11.68 μg m<sup>-3</sup> in winter, respectively. These values were approximately twice those at rural and urban summer sites as well as the tunnel environment. The average values of OC4 were 10.30 μg m<sup>-3</sup> and 15.19 μg m<sup>-3</sup> for rural winter and urban winter samples, respectively, which were much higher than those of rural summer (4.44 μg m<sup>-3</sup>) and urban summer (3.55 μg m<sup>-3</sup>) samples. Compared to those at rural and urban sites, much lower OC4 levels were observed in the tunnel environment (2.27 μg m<sup>-3</sup>).

EC1 was the dominant elemental carbon fraction at all sites in the present study. The average values of EC1 obtained in rural winter (23.78 μg m<sup>-3</sup>), urban winter (25.68 μg m<sup>-3</sup>) and tunnel (25.83 μg m<sup>-3</sup>) samples were comparable, and were much higher than those measured in rural summer (5.97 μg m<sup>-3</sup>) and urban summer (6.45 μg m<sup>-3</sup>) samples. The levels of EC2 in winter (0.69 μg m<sup>-3</sup> for rural and 0.53 μg m<sup>-3</sup> for urban) were twice as high as those in summer. The highest level of EC2 was observed in the tunnel environment (0.88 μg m<sup>-3</sup>). EC3 was almost under the method detection limit for tunnel, rural summer and urban summer samples. Nonetheless, a value of about 0.35 μg m<sup>-3</sup> for EC3 was observed in both the rural and urban winter samples. The lowest values for all carbon fractions were observed at the remote site with values below 0.5 μg m<sup>-3</sup>.

The highest level of OP was found for the rural winter samples, which ranged from 1.2 to 54.3 μg m<sup>-3</sup> with an average of 18.6 μg m<sup>-3</sup>. The average OP concentration in the urban winter samples was 6.4 μg m<sup>-3</sup> and ranged from 1.5 to 36 μg m<sup>-3</sup>. The levels of OP in winter were 6 times higher than those in summer at both the rural and urban sites. The average OP concentrations at the tunnel and remote sites were 4.9 and 0.16 μg m<sup>-3</sup> and ranged from 1.6 to 11.3 μg m<sup>-3</sup> and 0.1 to 0.47 μg m<sup>-3</sup>, respectively. The variations of OP, were attributed to the abundance of the water-soluble organic carbon portion (Yu et al., 2002). The results showed that OP was more abundant at rural sites than at any of the other sites.

**Table 1**  
Mass concentrations of the carbon fractions among various environments.

Sites	Conc. ( $\mu\text{g m}^{-3}$ )	OC1	OC2	OC3	OC4	OP	EC1	EC2	EC3
Rural (winter)	Min.	0.83	1.70	1.86	1.22	1.22	1.86	0.31	0.00
	Max.	21.45	18.52	17.37	18.19	54.25	63.97	1.26	0.93
	Ave.	6.79	9.93	10.84	10.30	18.57	23.78	0.69	0.39
	Stdev.	6.00	4.73	4.89	4.56	15.5	17.71	0.30	0.29
Rural (summer)	Min.	0.57	2.58	3.07	1.58	1.32	3.39	0.17	0.00
	Max.	1.15	7.84	9.90	8.64	4.84	9.73	0.53	0.27
	Ave.	0.79	4.11	5.19	4.44	3.08	5.97	0.30	0.04
	Stdev.	0.15	1.12	1.76	1.82	0.89	1.46	0.11	0.08
Urban (winter)	Min.	2.99	5.06	7.08	7.25	1.5	6.69	0.26	0.20
	Max.	12.66	17.38	18.97	27.82	36.0	72.84	0.79	0.55
	Ave.	6.19	10.12	11.68	15.19	6.36	25.68	0.53	0.35
	Stdev.	2.48	3.26	3.20	4.89	10.2	16.32	0.11	0.08
Urban (summer)	Min.	0.33	1.38	3.00	0.46	0.5	0.48	0.18	0.00
	Max.	3.92	4.93	7.96	7.56	2.9	12.68	0.63	0.40
	Ave.	2.64	3.42	4.80	3.55	1.17	6.45	0.35	0.08
	Stdev.	0.72	0.86	1.54	1.62	0.66	2.39	0.11	0.10
Tunnel	Min.	0.28	5.83	1.19	0.00	1.6	5.64	0.00	0.00
	Max.	16.39	15.27	8.50	4.64	11.3	58.84	2.01	0.02
	Ave.	10.22	8.35	5.08	2.27	4.9	25.83	0.88	0.00
	Stdev.	5.74	3.53	1.86	1.12	3.9	13.68	0.62	0.01
Remote	Min.	0.02	0.13	0.12	0.10	0.07	0.27	0.03	0.00
	Max.	0.07	0.43	0.45	0.68	0.47	0.76	0.14	0.20
	Ave.	0.03	0.21	0.23	0.26	0.16	0.48	0.09	0.03
	Stdev.	0.01	0.08	0.09	0.16	0.1	0.15	0.11	0.04

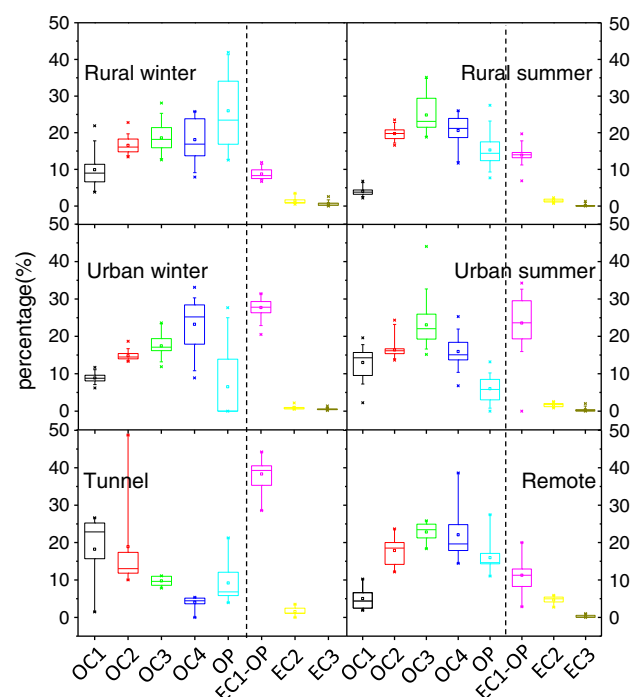
Overall, high levels of OC were found in the rural winter ( $56.43 \mu\text{g m}^{-3}$ ), urban winter ( $49.54 \mu\text{g m}^{-3}$ ) and tunnel samples ( $30.88 \mu\text{g m}^{-3}$ ). The lowest level was found at the remote site ( $0.90 \mu\text{g m}^{-3}$ ). The concentrations of OC in winter were three times higher than those in summer at both the rural and urban sites. The range of EC at the rural site was  $0.96\text{--}11.58 \mu\text{g m}^{-3}$  with an average of  $6.3 \mu\text{g m}^{-3}$  in winter, and  $1.99\text{--}6.03 \mu\text{g m}^{-3}$  with an average of  $3.23 \mu\text{g m}^{-3}$  in summer, respectively. The EC level in the urban environment varied from  $7.53$  to  $37.92 \mu\text{g m}^{-3}$  with an average of  $20.20 \mu\text{g m}^{-3}$  in winter and from  $0.22$  to  $10.23 \mu\text{g m}^{-3}$  with an average level of  $5.70 \mu\text{g m}^{-3}$  in summer, respectively. Compared to the warm season, the higher OC and EC concentrations in the rural winter and urban winter may be attributed to the local heating activities (including biomass burning and coal combustion). Attributing to the vehicle emissions and poor dilution conditions, the highest EC level was found in the tunnel environment with an average level of  $21.75 \mu\text{g m}^{-3}$ . The lowest EC value was found at the remote site ( $0.44 \mu\text{g m}^{-3}$ ).

### 3.2. The contributions of carbon fractions to TC among the sites

The carbon fraction contributions to TC are shown in Fig. 1. The percentages of OC1 to TC varied widely, and accounted for 5.0% of remote and 18.2% of tunnel TC. The contributions of OC2 to TC at all sites were comparable, and ranged from 14.8% (urban winter) to 19.8% (rural summer). The percentages of OC3 and OC4 to TC varied slightly with levels of 17.5% to 24.8% for OC3 and 15.9% to 23.2% for OC4 in the rural, urban and remote samples. Lower contributions of OC3 (9.8%) and OC4 (4.0%) to TC were observed at the tunnel site compared with those at the other sites. Considering the significant effect of the artifacts for OC1 and source sites (Chow et al., 2010; Watson et al., 2009), a comprehensive study of the contributions and artifacts is needed among various regions and seasons.

EC1–OP (char) accounted for 38% of TC in the tunnel samples, and in urban samples EC1–OP accounted for 27.7% and 23.6% in winter and summer, respectively. Compared to the tunnel and urban sites, a lower percentage of EC1–OP was found in the rural and remote samples. EC2 contributed less than 1.7% to TC in the rural, urban and tunnel samples, but a higher contribution (5%) was found in the remote samples. These results demonstrated high levels of char in the tunnel and urban environments, which was mainly due to the

richness of EC1 and a low level of OP in particles. Previous studies reported that EC1 was observed to be 99% of the EC for tire-wear (Aatmeeyata and Sharma, 2010). A high emission factor for EC from tire-wear was reported ( $1.46 \text{ mg tire}^{-1} \text{ km}^{-1}$ ) for small cars (Aatmeeyata and Sharma, 2010). Some studies also reported that tire-wear rates were in the range of  $6.6\text{--}90 \text{ mg tire}^{-1} \text{ km}^{-1}$ , and large annual emissions of tire-wear in the environment have been observed (Boulter, 2005; Allen et al., 2006; Aatmeeyata et al., 2009; Wik and Dave, 2009). Gray and Cass calculated that the attrition of tires led to an EC contribution of  $330 \text{ kg day}^{-1}$  and an OC contribution of  $1001 \text{ kg day}^{-1}$  for an area of  $3600 \text{ km}^2$  in Los Angeles (Gray and Cass, 1998). Furthermore, tire-wear may contribute considerable traffic emissions as the exhaust gasses have become cleaner following



**Fig. 1.** The percentage contributions of carbon fraction to total carbon among various sites.

the use of catalytic converters and improved fuels and engines (EMEP/CORINAIR, 2004).

In summary, the percentage profiles of carbon fractions were characterized by one peak (for rural and remote samples) and two peaks (for urban and tunnel samples), respectively. The highest peak corresponding to OC3 was found in rural summer and remote samples, and the rural winter peak was characterized by OP. The two peak profile with the highest EC1–OP and the second highest OC4 was found in urban winter samples, and the peaks in the urban summer samples were EC1–OP and OC3, respectively. A distinct contribution profile for the tunnel samples was observed with two peaks corresponding to EC1–OP and OC1. In addition, the profile for the tunnel samples showed a unique pattern (decreasing from OC1 to OC4, and a sharp increase in EC1–OP). These results indicated that the contributions of major sources to carbonaceous aerosols and the dilutions were different at the sites. Compared to the absolute concentration, the percentages of carbon fractions to TC reflected the properties of carbonaceous aerosols. Considering the thermal and optical effects of the eight carbon fractions, these results might provide some information for models used in radiative evaluation.

### 3.3. The distributions of POC, SOC, char and soot

As shown in Fig. 2, using the minimum OC/EC ratio method, OC was classified as primary organic carbon (POC) and secondary organic carbon (SOC) (Turpin and Huntzicker, 1995; Cao et al., 2003). EC was classified as char and soot (Han et al., 2009). The formation of SOC increases the ambient concentration of OC and the ambient OC/EC ratio. OC/EC ratios exceeding the expected primary emission ratio are an indication of SOC formation. Previous studies showed that the percentages of SOC to the total OC were different at various sites (Gray, 1986; Turpin and Huntzicker, 1995; Schauer et al., 1996). However, investigations into the contributions of POC, SOC, char and soot to TC at rural, urban, tunnel and remote sites synchronously are scarce.

The contributions of POC to TC were comparable in rural, urban and tunnel samples ranging from 46.3% to 57.8%, and were much higher than those for remote samples (16.4%). POC contributions to TC in remote samples were the lowest among the various sites. The contributions of SOC to TC varied widely, and ranged from 9.08% (tunnel) to 50.8% (remote). The highest contribution of SOC to TC was found at the remote site. This was due to a large contribution by aged aerosols resulting from long-range transport from the primary sources and a minor contribution from a local source. Given the tunnel microenvironment, fresh emissions from traffic-related sources (e.g., vehicle exhaust and tire-wear) had a major effect on the abundance of POC and the reduced production of SOC, therefore, the low contribution of SOC was reasonable.

The percentages of char to TC were discussed in Section 3.2. Compared to char, soot accounted for only a small fraction (less than 2%) of TC in the rural, urban and tunnel samples, but higher contributions were found in remote samples (~9%). The percentage profiles of char and soot indicated that char was more abundant in EC than soot. Furthermore, considering the various concentrations and percentages of POC, SOC, char and soot at the different sampling sites, it is important to consider the distributions of carbonaceous aerosols in radiative models. The small percentage of soot indicated that the soot was the background fraction in total EC, and it is worth noting that the higher percentage of soot in the remote area compared with the other sites might suggest that remote carbonaceous aerosols may have a greater contribution to radiative absorption per unit TC than at other sites. A previous study reported that the estimated contribution of carbonaceous aerosols to the earth's radiative budget is considerable, and is attributed to the uncertainties of emission inventories compounded by physical uncertainties and indirect effects (Forster et al., 2007). Therefore, further research into

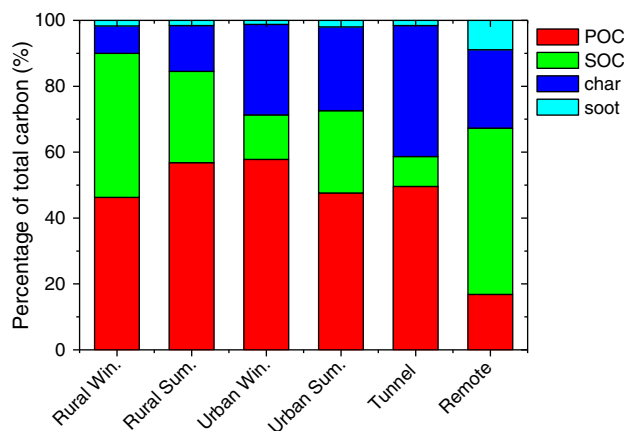


Fig. 2. Percentages of total carbon contributed by POC, SOC, char and soot for various sites.

carbonaceous fractions and the distributions of these fractions in various regions is one method of reducing these uncertainties.

### 3.4. Correlations between carbon fractions, OC/EC and char/soot

Table 2 shows the relationships between different carbon fractions (OC, EC, char and soot) and the ratios (OC/EC and char/soot). High correlations between OC and EC were observed in rural ( $R = 0.94$  in winter and  $R = 0.84$  in summer), urban ( $R = 0.97$  in winter and  $R = 0.78$  in summer) and tunnel ( $R = 0.97$ ) samples. A low correlation was found in remote samples ( $R = 0.52$ ). The significant correlations between OC and EC in rural, urban and tunnel samples suggested that OC and EC were derived largely from the same source (especially in rural winter, urban winter and the tunnel environments). The non-significant correlations between OC and EC in remote samples might be due to the abundance of SOC and the long-term evolution of aging aerosols.

As shown in Table 2, char had strong positive correlations with OC in rural winter, urban winter and tunnel samples, but not in remote samples. On the other hand, the strong correlations between char and EC indicated that char dominated total EC at all sites. These findings were consistent with previous results (Han et al., 2009, 2010; Kim et al., 2011). The formation of soot partly increased as the formation of OC and EC increased from the same sources at all sites (especially at the rural winter and remote sites), because soot showed positive correlations with OC and EC. The relationships between char and soot in rural winter samples was linear and highly correlated ( $R = 0.80$ ). The rural summer samples showed a low correlation between char and soot. Differences in local and regional contributors and neutral atmospheric conditions with a high mixing height in summer may have led to the non-significant correlation between char and soot. For samples collected at the urban site, soot and char showed low correlation coefficients, especially for urban summer samples. These results suggested that the contributions by char and soot were more complicated considering the mixing sources including vehicle emissions, coal combustion, biomass burning and the re-suspended road dust. The observed low correlations between char and soot in the tunnel and remote samples further indicated that char and soot represented different species and were produced from both fresh emissions and aged aerosols. Positive and negative correlations between the ratios (OC/EC and char/soot) and carbon fractions will be discussed in Section 3.5.

### 3.5. The variations in OC/EC and char/soot ratios between the sites

The ratios of OC/EC were used to determine emissions, aging evolution and the presence of secondary organic aerosols although there were some limitations for the method (Chow et al., 1993;

**Table 2**  
Relationships among carbonaceous species and ratios (R).

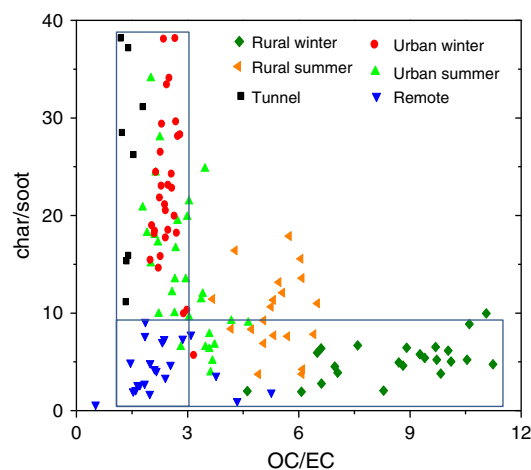
	Rural win. (n = 23)	Rural sum. (n = 23)	Urban win. (n = 30)	Urban sum. (n = 31)	Tunnel (n = 9)	Remote (n = 22)
OC vs EC	0.94	0.84	0.97	0.78	0.97	0.58
OC vs char	0.95	0.51	0.97	0.70	0.97	0.34
OC vs soot	0.71	0.27	0.34	0.50	0.53	0.88
EC vs char	0.99	0.99	0.99	0.99	0.99	0.95
EC vs soot	0.86	0.43	0.31	0.29	0.59	0.73
Char vs soot	0.80	0.29	0.29	0.12	0.55	0.49
OC/EC vs OC	0.68	0.50	0.20	−0.41	−0.68	0.64
OC/EC vs EC	0.43	−0.46	−0.04	−0.88	−0.75	−0.48
Char/soot vs char	0.22	0.24	0.80	0.64	0.12	0.12
Char/soot vs soot	−0.37	−0.76	−0.31	−0.59	−0.77	−0.45

n: number of the samples.

Zeng and Wang, 2011). In addition, the ratios of char/soot have also been reported as another index in carbonaceous aerosol research (Han et al., 2010). The present study is the first to characterize and compare the ratios of OC/EC and char/soot at various sites (including rural, urban, tunnel and remote environments) (Fig. 3).

The average ratios of OC/EC and char/soot for rural winter samples were  $8.6 \pm 1.8$  and  $5.2 \pm 1.9$ , respectively. Compared to winter samples, lower OC/EC ratios were observed in rural summer samples ( $5.4 \pm 0.8$ ). However, the values of char/soot ( $10.1 \pm 3.4$ ) in rural summer samples were much higher than those in rural winter samples. OC/EC ratios in urban winter samples were composed to unity ( $2.5 \pm 0.3$ ) than those for char/soot ( $22.1 \pm 7.9$ ). Higher OC/EC ratios were found in urban summer samples with an average value of  $2.9 \pm 0.7$  compared to winter samples, which demonstrated the abundance of secondary organic aerosols in summer. The char/soot ratios in urban summer samples, however, were lower than those in urban winter samples with an average value of 14.4. The OC/EC ratios in urban samples were similar to the ratios calculated from emission inventories of China (Cao et al., 2005), which may reflect the combined contributions from coal combustion, traffic-related emissions, and biomass burning for urban OC and EC. The ratios of char/soot in urban samples were slightly higher than those found in the study by Han et al. (ratios above 10 were also observed during winter), which were attributed to the different sampling periods (Han et al., 2010). The average OC/EC value for the tunnel site ( $1.6 \pm 0.4$ ) was lower than those measured at the other sites in the present study, demonstrating the dominant influence of fresh vehicle exhaust, for which the OC/EC ratios are known to be low. The variations in char/soot ratios in the tunnel samples ( $25.5 \pm 10.3$ ) were similar with those in the urban winter samples. As shown in Fig. 3, the ratios of OC/EC ( $2.3 \pm 1.0$ ) and char/soot ( $4.3 \pm 2.5$ ) in the remote samples were lower than those at the other sites, with the exception of the OC/EC ratio at the tunnel site.

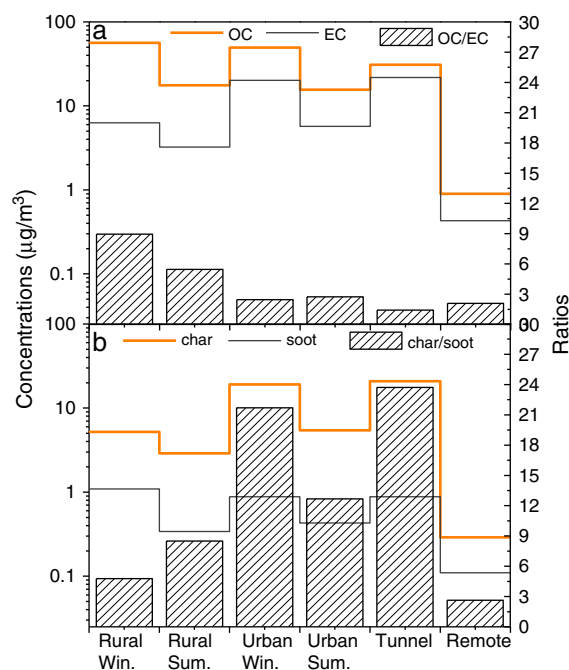
In general, the results showed that the urban OC/EC ratios were always slightly lower in winter than in summer, which is mainly due to more secondary organic carbon production in summer. Compared to the urban site, high OC/EC ratios at the rural site indicated the significant contributions of biomass burning (especially in the heating season). The concentrations of EC at the urban site were significantly increased in winter, however, no corresponding seasonal change in OC/EC ratios was observed. Compared to the rural samples, seasonal OC/EC variations in the urban samples were less pronounced. These results showed that the aerosol-containing components susceptible to charring (e.g., water-soluble organic compounds) had higher OC/EC variability (rural samples) compared to diesel-impacted aerosols (urban and tunnel samples) (Yu et al., 2002). The OC/EC ratios fluctuated more in the rural winter, rural



**Fig. 3.** The distributing profile of OC/EC and char/soot.

summer and urban summer samples than in the urban winter, tunnel and remote samples. Nonetheless, the ratios of char/soot at the tunnel and urban sites fluctuated more than those at the remote and rural sites, which indicated the variations in dominant contributors. In addition, the OC/EC ratios were affected by episodes of biomass burning and SOC production. These results indicated that the two ratios might be different effective indicators in source identification at various sites.

The average levels of OC, EC, char and soot as well as the ratios of OC/EC and char/soot in the various ambient samples are shown in Fig. 4. Due to the larger contribution from biomass burning emission with rich OC at the rural site, high OC/EC ratios and relatively high concentrations of OC (especially in winter) were found, which was confirmed by the positive correlation between OC/EC and OC ( $R = 0.68$ ). The relatively low OC/EC ratio in rural summer samples was a result of decreased OC compared with EC. The ratios of OC/EC in the tunnel and urban winter samples were mainly due to the high level of EC compared with OC, and negative correlations between OC/EC and EC were observed ( $R$  values were  $-0.88$  and  $-0.75$  for urban summer



**Fig. 4.** Levels of carbon species and the ratios (a: for OC, EC and OC/EC; b: for char, soot and char/soot).

and tunnel samples, respectively). The high ratios of char/soot in urban winter and tunnel samples may have been due to the abundance of char in tunnel and urban samples (e.g.,  $R = 0.80$  for urban winter samples) and the relatively low soot levels ( $R = -0.31$  for urban winter and  $R = -0.77$  for tunnel samples). The correlations between the char/soot ratios and both char and soot in urban summer samples were 0.64 and  $-0.59$ , respectively.

High char levels in the tunnel samples was mainly due to the traffic-related sources and poor dilution conditions, and char levels in urban winter samples were associated with complex sources (including biofuel use and traffic-related emissions) (Fig. 4). The possibility of char emission by traffic emissions has been reported in a previous study, which showed high concentrations of char in urban areas and heavily trafficked roads (Kim et al., 2011). Nevertheless, the possibility that diesel engines emit char or char-like particulates via incomplete combustion is unlikely to fully explain the significantly high level observed. Han et al. reported that char is emitted largely from biomass burning and coal combustion, and not from vehicle exhaust (Han et al., 2009, 2010). It is reasonable that the high levels of char in the tunnel and urban environments were partly due to the abundance of tire-wear and low level of OP in particles. These conclusions are also consistent with previous studies, which reported that traffic-related tire-wear is a significant source of OC and EC (99% EC1) (Hildemann et al., 1991; Schauer et al., 1996; Dahl et al., 2006; Thorpe and Harrison, 2008; Aatmeeyata and Sharma, 2010).

#### 4. Conclusions

The characteristics of eight carbon fractions, OC/EC and char/soot ratios at rural, urban, tunnel and remote sites were investigated. The highest level of OC1 was found at the tunnel site with  $10.22 \mu\text{g m}^{-3}$  due to fresh vehicle exhaust and poor dilution conditions. The levels of OC2–3 in the rural and urban environments were twice as high in winter as those in summer. Compared to rural and urban sites, OC4 levels were much lower in the tunnel environment. EC1 was the dominant elemental carbon fraction at all sites in the present study. The lowest level of carbon fractions was observed in the remote samples and was below  $0.5 \mu\text{g m}^{-3}$ .

The profiles of carbon fractions to TC were characterized by one peak (at rural and remote sites) and two peaks (at urban and tunnel sites) with different carbon fractions, respectively. POC made a significant contribution (~50%) to TC in rural, urban and tunnel environments, while the lowest level was found in remote samples (16.4%). SOC contributed least to TC at 9.08% and the highest level was 50.8% at the tunnel and remote sites, respectively. Our results showed that the ratios of OC/EC and char/soot were different effective indicators of source identification in the various environments. The distinctive carbonaceous fractions in different environments also provide indications in estimating their effects on climate by models.

#### Conflict of interest

The authors declare no conflict of interest.

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#### References

Aatmeeyata, Sharma M. Polycyclic aromatic hydrocarbons, elemental and organic carbon emissions from tire-wear. *Sci Total Environ* 2010;408:4563–8.

- Aatmeeyata, Kaul DS, Sharma M. Traffic generated non-exhaust particulate emissions from concrete pavement: a mass and particle size study for two-wheelers and small cars. *Atmos Environ* 2009;43:5691–7.
- Allen JO, Alexandrove O, Kaloush KE. Tyre wear emissions for asphalt rubber and Portland cement concrete pavement surfaces. Arizona Department of Transportation; 2006 [Contract KR-04-0720-TRN].
- Boulter PG. A review of emission factors and models for road vehicle non-exhaust particulate matter. TRL 2005; PPR065; report prepared for DEFRA. Northern Ireland; 2005.
- Cao JJ, Lee SC, Ho KF, Zhang XY, Zou SC, Fung K, et al. Characteristics of carbonaceous aerosol in Pearl River Delta Region, China during 2001 winter period. *Atmos Environ* 2003;37:1451–60.
- Cao JJ, Wu F, Chow JC, Lee SC, Li Y, Chen SW, et al. Characterization and source apportionment of atmospheric organic and elemental carbon during fall and winter of 2003 in Xi'an, China. *Atmos Chem Phys* 2005;5:3127–37.
- Cao JJ, Lee SC, Chow JC, Watson JG, Ho KF, Zhang RJ, et al. Spatial and seasonal distributions of carbonaceous aerosols over China. *J Geophys Res* 2007;112: D22S11. <http://dx.doi.org/10.1029/2006JD008205>.
- Cao JJ, Zhu CS, Chow JC, Watson JG, Han YM, Wang GH, et al. Black carbon relationships with emissions and meteorology in Xi'an, China. *Atmos Res* 2009;94: 194–202.
- Chen SC, Tsai CJ, Chou CCK, Roam GD, Cheng S-S, Wang Y-N. Ultrafine particles at three different sampling locations in Taiwan. *Atmos Environ* 2010;44:533–40.
- Chow JC, Watson JG, Pritchett LC, Pierson WR, Frazier CA, Purcell RG. The DRI thermal optical reflectance carbon analysis system-description, evaluation and applications in United-States Air-Quality Studies. *Atmos Environ* 1993;27A: 1185–201.
- Chow JC, Watson JG, Chen LWA, Chang MCO, Robinson NF, Trimble D, et al. The IMPROVE-A temperature protocol for thermal/optical carbon analysis: maintaining consistency with a long-term database. *J Air Waste Manage Assoc* 2007;57:1014–23.
- Chow JC, Watson JG, Chen LWA, Rice J, Frank NH. Quantification of  $\text{PM}_{2.5}$  organic carbon sampling artifacts in US networks. *Atmos Chem Phys* 2010;10: 5223–39.
- Chow JC, Watson JG, Robles J, Wang X, Chen LW, Trimble DL, et al. Quality assurance and quality control for thermal/optical analysis of aerosol samples for organic and elemental carbon. *Anal Bioanal Chem* 2011;401:3141–52.
- Dahl A, Gharibi A, Swietlicki E, Gudmundsson A, Bohgard M, Ljungman A, et al. Traffic generated emissions of ultrafine particles from pavement-tire interface. *Atmos Environ* 2006;40:1314–23.
- EMEP/CORINAIR. Emission inventory guidebook—3rd edition update. European Environment Agency; 2004 [September].
- Feng Y, Chen Y, Guo H, Zhi G, Xiong S, Li J, et al. Characteristics of organic and elemental carbon in  $\text{PM}_{2.5}$  samples in Shanghai, China. *Atmos Res* 2009;92:434–42.
- Forster P, Ramaswamy V, Artaxo P, Bernsten T, Betts R, Fahey DW, et al. Changes in atmospheric constituents and in radiative forcing. In: Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, Tignor M, Miller HL, editors. *Climate change 2007: the physical science basis. Contribution of working group I to the fourth assessment report of the Intergovernmental Panel on Climate Change*; 2007.
- Grabowsky J, Streibel T, Sklorz M, Chow JC, Watson JG, Mamakos A, et al. Hyphenation of a carbon analyzer to photo-ionization mass spectrometry to unravel the organic composition of particulate matter on a molecular level. *Anal Bioanal Chem* 2011;401: 3153–64.
- Gray HA. Ph.D. Thesis, Pasadena, CA: California Institute of Technology, 1986.
- Gray HA, Cass GR. Source contributions to atmospheric fine carbon particle concentrations. *Atmos Environ* 1998;32:3805–25.
- Han YM, Lee SC, Cao JJ, Ho KF, An ZS. Spatial distribution and seasonal variation of char-EC and soot-EC in the atmosphere over China. *Atmos Environ* 2009;43: 6066–73.
- Han YM, Cao JJ, Lee SC, Ho KF, An ZS. Different characteristics of char and soot in the atmosphere and their ratio as an indicator for source identification in Xi'an, China. *Atmos Chem Phys* 2010;10:595–607.
- Hildemann LM, Markowski GR, Cass GR. Chemical composition of emissions from urban sources of fine organic aerosol. *Environ Sci Technol* 1991;25:744–59.
- Jacobson MZ. Effects of externally-through-internally-mixed soot inclusions within clouds and precipitation on global climate. *J Phys Chem A* 2006;110: 6860–73.
- Kim KH, Sekiguchi K, Kudo S, Sakamoto K. Characteristics of atmospheric elemental carbon (char and soot) in ultrafine and fine particles in a roadside environment, Japan. *Aerosol Air Qual Res* 2011;11:1–12.
- Kopp RE, Mauzerall DL. Assessing the climatic benefits of black carbon mitigation. *Proc Natl Acad Sci* 2010;107:11703–8.
- Poschl U. Atmospheric aerosol: composition, transformation, climate and health effects. *Angew Chem Int Ed Engl* 2005;44(46):7520–40.
- Satsangi A, Pachauri T, Singla V, Lakhani A, Kumari KM. Organic and elemental carbon aerosols at a suburban site. *Atmos Res* 2012;113:13–21.
- Schauer JJ, Rogge WF, Hildemann LM, Mazurek MA, Cass GR. Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmos Environ* 1996;30:3837–55.
- Schmidl C, Marr IL, Caseiro A, Kotianová P, Berner A, Bauer H, et al. Chemical characterisation of fine particle emissions from wood stove combustion of common woods growing in mid-European Alpine regions. *Atmos Environ* 2008;42:126–41.
- Schwarz J, Chi X, Maenhaut W, Civiš M, Hovorka J, Smolík J. Elemental and organic carbon in atmospheric aerosols at downtown and suburban sites in Prague. *Atmos Res* 2008;90:287–302.

- Shen ZX, Cao JJ, Arimoto R, Zhang RJ, Jie DM, Liu SX, et al. Chemical composition and source characterization of spring aerosol over Horqin sand land in northeastern China. *J Geophys Res* 2007;112:D14315. <http://dx.doi.org/10.1029/2006JD007991>.
- Thorpe A, Harrison RM. Sources and properties of non-exhaust particulate matter from road traffic: a review. *Sci Total Environ* 2008;400:270–82.
- Turpin BJ, Huntzicker JJ. Identification of secondary aerosol episodes and quantification of primary and secondary organic aerosol concentrations during SCAQS. *Atmos Environ* 1995;29:3527–44.
- Wang XH, Bi XH, Sheng GY, Fu JM. Chemical composition and sources of PM<sub>10</sub> and PM<sub>2.5</sub> aerosols in Guangzhou, China. *Environ Monit Assess* 2006;119:425–39.
- Watson JG, Chow JC, Chen LWA, Frank NH. Methods to assess carbonaceous aerosol sampling artifacts for IMPROVE and other long-term networks. *J Air Waste Manage Assoc* 2009;59:898–911.
- Wik A, Dave G. Occurrence and effects of tire wear particles in the environment—a critical review and an initial risk assessment. *Environ Pollut* 2009;157:1–11.
- Yu JZ, Xu JH, Yang H. Charring characteristics of atmospheric organic particulate matter in thermal analysis. *Environ Sci Technol* 2002;36:754–61.
- Zeng T, Wang Y. Nationwide summer peaks of OC/EC ratios in the contiguous United States. *Atmos Environ* 2011;45:578–86.
- Zhang RJ, Fu CB, Han ZW, Zhu CS. Characteristics of elemental composition of PM<sub>2.5</sub> in the spring period at Tongyu in the semi-arid region of Northeast China. *Adv Atmos Sci* 2008;25:922–31.
- Zhang RJ, Ho KF, Cao JJ, Han ZW, Zhang MG, Cheng Y, et al. Organic carbon and elemental carbon associated with PM<sub>10</sub> in Beijing during spring time. *J Hazard Mater* 2009;172:970–7.
- Zhu CS, Chen CC, Cao JJ, Tsai CJ, Chou CCK, Liu SC, et al. Characterization of carbon fractions for atmospheric fine particles and nanoparticles in a highway tunnel. *Atmos Environ* 2010;44:2668–73.
- Zhu CS, Cao JJ, Shen ZX, Liu SX, Zhang T, Zhao ZZ, et al. The indoor and outdoor chemical components of PM<sub>2.5</sub> in rural area of Northwestern China—case study. *Aerosol Air Qual Res* 2012a;12:1157–65.
- Zhu CS, Tsai CJ, Chen SC, Cao JJ, Roam GD. Positive sampling artifacts of organic carbon fractions for fine particles and nanoparticles in a tunnel environment. *Atmos Environ* 2012b;54:225–30.