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Characterization and source apportionment of atmospheric organic and elemental carbon during fall and winter of 2003 in Xi'an, China

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Abstract. Continuous measurements of atmospheric organic and elemental carbon (OC and EC) were taken during the high-pollution fall and winter seasons at Xi'an, Shaanxi Province, China from September 2003 through February 2004. Battery-powered mini-volume samplers collected $PM_{2.5}$ samples daily and PM_{10} samples every third day. Samples were also obtained from the plumes of residential coal combustion, motor-vehicle exhaust, and biomass burning sources. These samples were analyzed for OC/EC by thermal/optical reflectance (TOR) following the Interagency Monitoring of Protected Visual Environments (IMPROVE) protocol. OC and EC levels at Xi'an are higher than most urban cities in Asia. Average $PM_{2.5}$ OC concentrations in fall and winter were $34.1\pm18.0\,\mu g\,m^{-3}$ and $61.9\pm33.2\,\mu g\,m^{-3}$, respectively; while EC concentrations were $11.3\pm6.9\,\mu g\,m^{-3}$ and $12.3\pm5.3\,\mu g\,m^{-3}$, respectively. Most of the OC and EC were in the $PM_{2.5}$ fraction. OC was strongly correlated (R>0.95) with EC in the autumn and moderately correlated (R=0.81) with EC during winter. Carbonaceous aerosol (OC×1.6+EC) accounted for 48.8%±10.1% of the $PM_{2.5}$ mass during fall and 45.9±7.5% during winter. The average OC/EC ratio was 3.3 in fall and 5.1 in winter, with individual OC/EC ratios nearly always exceeding 2.0. The higher wintertime OC/EC corresponded to increased residential coal combustion for heating. Total carbon (TC) was associated with source contributions using absolute principal component analysis (APCA) with eight thermally-derived carbon fractions. During fall, 73% of TC was attributed to gasoline engine exhaust, 23% to diesel exhaust, and 4% to biomass burning. During winter, 44% of TC was attributed to gasoline engine exhaust, 44% to coal burning, 9% to biomass burning, and 3% to diesel engine exhaust.

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1 Introduction

This study examines temporal variations of $PM_{2.5}$ and PM_{10} concentrations of organic and elemental carbon (OC and EC) in Xi'an, China. ($PM_{2.5}$ is particulate matter with an aerodynamic diameter smaller than 2.5 micrograms [μm], PM_{10} is particulate matter with an aerodynamic diameter smaller than 10 μm). This study also quantifies contributions of organic and elemental carbon in Xi'an from coal combustion, vehicle exhaust, fugitive dust and dust storms (Cao et al., 2005; Gao et al., 1997; Zhang et al., 1993; Zhuang et al., 1992).

With a population of five million, Xi'an, in Shaanxi Province, is the largest city in northwestern China. It has served as the capital city of 13 Chinese dynasties for more than a millennium. Since the discovery in 1974 of hundreds of buried life-size terra-cotta figures of warriors and horses, the city has been a major tourist attraction. Xi'an also experiences some of the worst air pollution among China's cities (Zhang et al., 2001, 2002), where elevated carbonaceous aerosol components contribute to high PM levels. Several studies have been conducted in China's well-developed coastal cities, such as Beijing, Shanghai, Guangzhou, and Hong Kong (Cao et al., 2003, 2004; He et al., 2001; Louie et al., 2005a, b; Ye et al., 2003), but few measurements are available from inland cities, such as Xi'an.

OC and EC in suspended particulate matter (PM) play important roles in health, visibility, and climate effects (ACE-Asia, 1999; Cooke et al., 1999; IPCC, 2001; UNEP and NOAA, 2003; Vedal, 1997; Watson, 2002). EC, which is

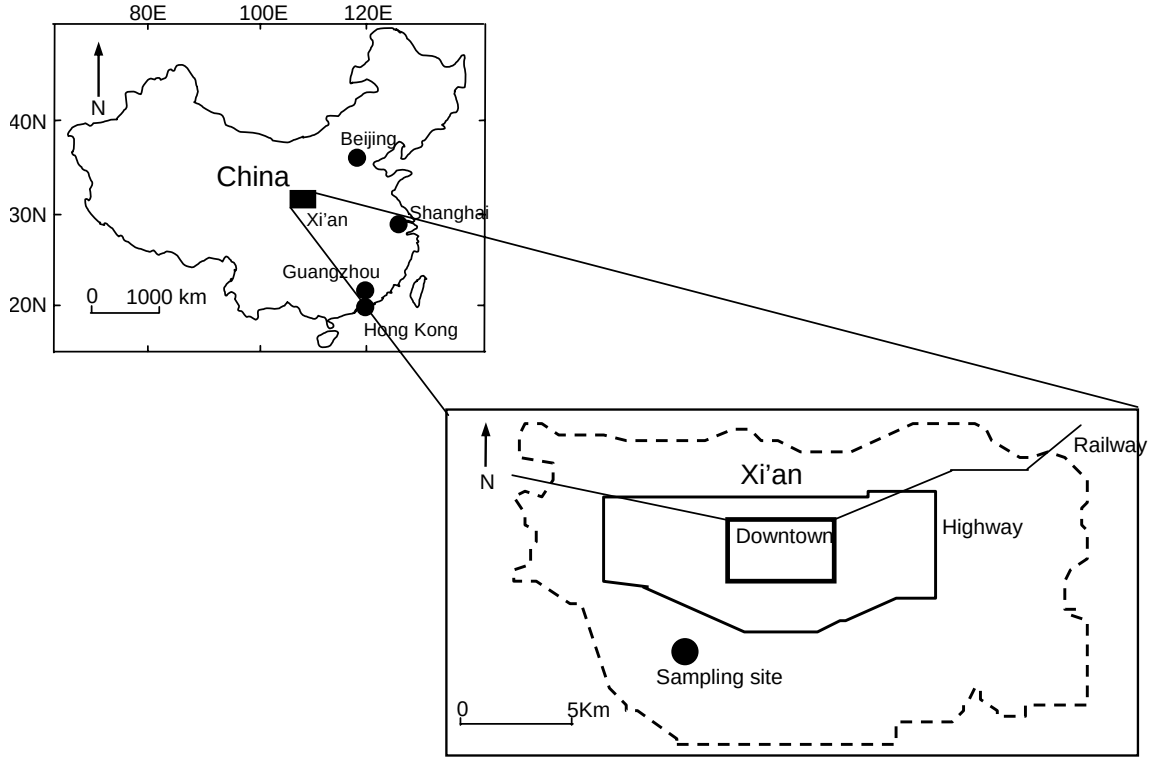

Fig. 1. Location of the sampling site at Xi'an, China.

often equated with optically-derived, light-absorbing black carbon (BC), is known to cause heating in the air on a regional scale, thus altering atmospheric stability and vertical mixing, and affecting large-scale circulation and the hydrologic cycle (Menon et al., 2002). Since about one fourth of global BC emissions are believed to originate from China (Cooke et al., 1999), a reduction of BC emissions in China could produce positive consequences for global warming (Jacobson, 2002).

2 Sampling and analysis

2.1 Sampling site

Xi'an is located on the Guanzhong Plain at the south edge of the Loess Plateau 400 m above sea level at 33°29′–34°44′ N, 107°40′–109°49′ E (Fig. 1). The monitoring site was located in an urban-scale zone of representation (Chow et al., 2002) surrounded by a residential area ∼15 km south of downtown Xi'an, where there are no major industrial activities, nor local fugitive dust sources. $PM_{2.5}$ and PM_{10} samples were obtained from 13 September 2003 to 29 February 2004 from the rooftop of the Chinese Academy of Sciences' Institute of Earth Environment building at 10 m above ground. Based on local meteorological characteristics and the residential heating season (mid-November through February), the period from 13 September 2003 to 31 October 2003 was designated as fall, and the period from 1 November 2003 to 29 February 2004 was designated as winter.

2.2 Sample collection

Daily $PM_{2.5}$ and every-third-day PM_{10} samples were collected using two battery-powered mini-volume samplers (Airmetrics, Oregon, USA) operating at flow rates of 5 liters per minute ($L\,min^{-1}$; Cao, 2003). Prior to field operations, calibrated MiniVol samplers were collocated with low volume $PM_{2.5}$ and PM_{10} Partisol samplers (model 2000, Rupprecht & Patashnick, Albany, New York, USA) at the Hong Kong Polytechnic University. The difference between the two types of samplers was less than 5% for the $PM_{2.5}$ and PM_{10} mass.

PM samples were collected on 47 mm Whatman quartz microfiber filters (QM/A) that were pre-heated at 900°C for three hours before sampling. The exposed filters were stored in a refrigerator at ∼4°C before chemical analysis to minimize the evaporation of volatile components. Quartz-fiber filters were analyzed gravimetrically for mass concentrations using a Sartorius MC5 electronic microbalance with a $\pm 1\,\mu g$ sensitivity (Sartorius, Göttingen, Germany) after 24-h equilibration at a temperature between 20°C and 23°C and a relative humidity (*RH*) between 35% and 45%. Each filter was weighed at least three times before and after sampling, and the net mass was obtained by subtracting the

Table 1. Average of OC and EC concentrations during September 2003 to February 2004 at Xi'an, China.

Season	Month	Sample numbers		OC[a]		EC		OC/EC	
		$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}
Fall	September	18	6	24.9±10.3[b]	29.6±11.2	8.3±4.5	11.0±6.4	3.3	3.0
	October	31	11	39.4±19.4	50.7±30.6	13.1±7.5	17.2±12.2	3.4	3.3
	Average			34.1±18.0	43.2±27.1	11.3±6.9	15.0±10.7	3.3	3.2
Winter	November	27	8	52.4±27.1	67.5±25.7	12.1±5.1	19.8±8.2	4.3	3.6
	December	29	8	81.7±36.2	124.8±54.8	15.2±4.6	28.9±8.9	5.3	4.3
	January	31	11	63.9±36.0	80.3±42.4	10.1±5.8	16.1±8.8	6.4	5.1
	February	29	9	48.6±21.7	98.7±87.6	12.0±4.4	26.8±18.2	4.1	3.5
	Average			61.9±33.2	93.0±58.4	12.3±5.3	22.7±12.3	5.1	4.2

[a] unit is $\mu g\,m^{-3}$
[b] values represent average ± standard deviation

average of pre-sampling weights from the average of post-sampling weights. Differences among replicate weighings were $<10\,\mu g$ for blanks and $<20\,\mu g$ for samples. Sixteen field blanks were collected to correct for adsorbed gas-phase organic components. Volatilization of particle-phase organics during and immediately after sampling was not quantified. A total of 165 $PM_{2.5}$ and 53 PM_{10} samples were collected during the ambient sampling period. Five $PM_{2.5}$ source samples were collected from residential stoves burning coal, six from alongside a major highway with heavy traffic, and five from smoke plumes when maize residue was burned after harvest.

Meteorological data were monitored continuously with a HFY-IA Wind Speed/Wind Direction Instrument (Changchun Institute of Metrological Instruments, Changchun, Jilin Province, China).

2.3 Thermal/optical carbon analysis

A $0.5\,cm^2$ punch from each samples was analyzed for OC and EC with a Desert Research Institute (DRI) Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, USA) for eight carbon fractions following the IMPROVE (Interagency Monitoring of Protected Visual Environments) thermal/optical reflectance (TOR) protocol (Chow et al., 1993, 2001, 2004a, 2005; Fung et al., 2002). This produces four OC fractions (OC1, OC2, OC3, and OC4 at 120°C, 250°C, 450°C, and 550°C, respectively, in a He atmosphere); a pyrolyzed carbon fraction (OP, determined when a reflected laser light attained its original intensity after O_2 was added to the analysis atmosphere); and three EC fractions (EC1, EC2, and EC3 at 550°C, 700°C, and 800°C, respectively, in a 2% O_2/98% He atmosphere). IMPROVE OC is defined as OC1+OC2+OC3+OC4+OP and EC is defined as EC1+EC2+EC3−OP. Inter-laboratory comparisons of samples between IMPROVE protocol with the DRI Model 2001 instrument and the TMO (thermal manganese dioxide oxidation) method (done by AtmAA, Inc., Calabasas, CA) has shown a difference of <5% for total carbon (TC) and 10% for OC/EC (Fung et al., 2002). Comparisons with other OC/EC methods (Watson et al., 2005) show that IMPROVE_TOR OC and EC are near the middle of the distribution of differences for the average of all methods. Average field blanks were 1.56 and $0.42\,\mu g\,m^{-3}$ for OC and EC, respectively. Quality Assurance/Quality Control (QA/QC) procedures have been described in Cao et al. (2003).

3 Results and discussion

3.1 Temporal variations of OC and EC

Monthly and seasonally averaged OC/EC concentrations are summarized in Table 1. $PM_{2.5}$ OC and EC during winter were 1.8 and 1.1 times, respectively, of those during fall; while. PM_{10} OC and EC during winter were 2.2 and 1.5 times, respectively, of those during fall. Monthly average OC and EC were highest during December and lowest during September. In December, OC in $PM_{2.5}$ and PM_{10} were $81.7\pm36.2\,\mu g\,m^{-3}$ and $124.8\pm54.8\,\mu g\,m^{-3}$, respectively; and EC in $PM_{2.5}$ and PM_{10} were $15.2\pm4.6\,\mu g\,m^{-3}$ and $28.9\pm8.9\,\mu g\,m^{-3}$, respectively. The maximum-to-minimum ratios for $PM_{2.5}$ and $PM_{10,}$ were 3.3 and 4.2 for OC and 1.8 and 2.6 for EC, respectively. Higher variability for OC concentrations may be due to the contributions of different emission sources.

Figure 2 shows that temporal variations of $PM_{2.5}$ OC coincided with mass and, to a lesser extent, with EC. OC was highly correlated with $PM_{2.5}$ (r=0.96, significance level 99%) and EC was moderately correlated with $PM_{2.5}$ (r=0.72, significance level 99%). $PM_{2.5}$ OC increased gradually from September to November, and reached a maximum on 14 December 2003 ($189.6\,\mu g\,m^{-3}$). Major emission sources of OC and EC in China include coal combustion (mostly

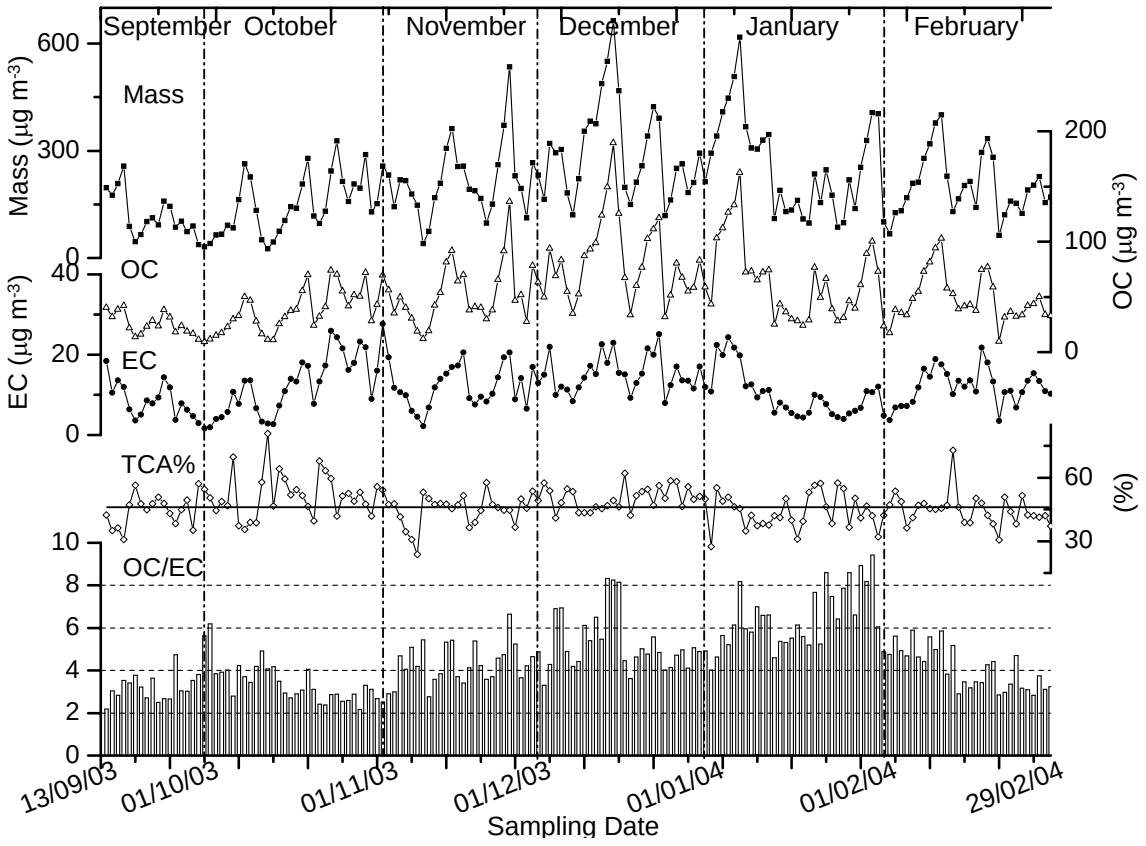

Fig. 2. Time series of $PM_{2.5}$ mass, organic carbon (OC), elemental carbon (EC), fraction of $PM_{2.5}$ composed of OC×1.6+EC (TCA%), and OC/EC ratios at Xi'an from 13 September 2003 to 29 February 2004. OC is multiplied by 1.6 for the TCA% calculation to account for unmeasured hydrogen and oxygen in organic material (Turpin and Lim, 2001).

residential), motor-vehicle exhaust, and biomass burning (Streets et al., 2001; Zhang et al., 2001), all of which are also evident in Xi'an. During the fall harvest season in mid-October, the residues of diverse crops like corn and rice are burned. Biofuels are also used by farmers for residential heating and cooking for both fall and winter. Zhang et al. (2001) showed that total suspended particle (TSP) in Xi'an reaches maximum levels in winter and minimum levels in summer. After the Chinese Spring Festival (22 January 2004 to 29 January 2004), OC decreases rapidly initially, then decreases further as February progresses. A similar trend was found for EC, but while EC concentration was lowest during the festival, it fluctuated at low values from 22 January 2004 to 5 February 2004.

3.2 Relationship between OC and EC

OC/EC ratios give some indication of the origins of carbonaceous $PM_{2.5}$ (Chow et al., 1996; Gray et al., 1986; Turpin and Huntzicker, 1991). As shown in Fig. 3, strong OC/EC correlations (0.95–0.97) in fall suggest impacts from a combination of common source contributions (i.e. residential and commercial coal combustion, biomass burning, motor-vehicle exhaust). OC/EC correlations (0.81) were lower in winter, consistent with a changing mixture of source contributions. Residential coal combustion was estimated to contribute more than 50% of TSP in 1997 (Zhang, 2001). Even though many residents in Xi'an have replaced coal with natural gas, a large number of low-income families still use coal for cooking and heating. Coal-fired boilers have been banned within the second beltway in downtown Xi'an since 1998, but due to the low cost of coal, many middle- and small-scale boilers are still in use.

The slopes of OC versus EC in winter were 5.12 for $PM_{2.5}$ and 3.83 for PM_{10}, compared to those in fall (2.46) (Fig. 3), implying that OC emissions in winter increased relative to EC emissions. The difference may be ascribed to the change of emission sources between the two seasons, primarily due to the completion of burning in corn and rice fields.

3.3 Variability of OC/EC ratios

OC/EC ratios are influenced by: 1) emission sources; 2) secondary organic aerosol (SOA) formation; and 3) different OC/EC removal rates by deposition (Cachier et al., 1996). Atmospheric EC is directly emitted, while OC can be both

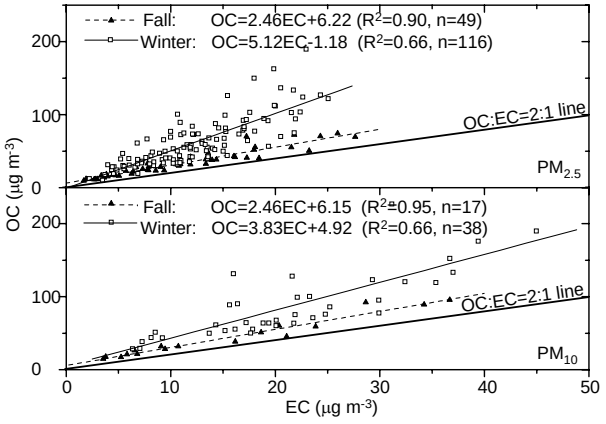

Fig. 3. Relationships between OC and EC concentrations in $PM_{2.5}$ and PM_{10}.

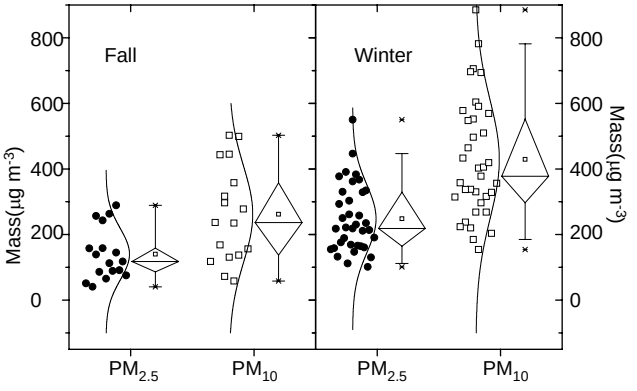

Fig. 4. Distribution of $PM_{2.5}$ and PM_{10} mass concentrations during fall and winter. The valid paired samples were 17 in fall and 36 in winter. The box plots indicate the mean 24-h concentration and the min, 1st, 25th, 50th, 75th, 99th and max percentiles. A normal curve is fitted to the measurements.

directly emitted and formed in the atmosphere from the low vapor pressure products of chemical reactions involving emissions of volatile organic compounds (VOCs).

As shown in Table 1, monthly averaged OC/EC ratios in $PM_{2.5}$ and PM_{10} ranged from 3.0 to 3.4 in fall, and 3.6 to 6.4 in winter. The highest ratios were recorded in January, with 6.4 in $PM_{2.5}$ and 5.1 in PM_{10}. Daily variations of $PM_{2.5}$ OC/EC ratios in Fig. 2 show lower ratios and variability in fall and higher ratios and variability in winter.

Regarding source samples, the average OC/EC ratio was 12.0 for coal-combustion, 4.1 for vehicle exhaust, and 60.3 for biomass burning. These ratios are much higher than reported values elsewhere of 2.7 for coal-combustion and 1.1 for motor vehicles (Watson et al., 2001), and 9.0 for biomass burning (Cachier et al., 1989). The individual OC/EC ratios for this study exceeded 2.0 for both $PM_{2.5}$ and PM_{10} fractions (Fig. 2), which might reflect the combined contributions from coal combustion, motor-vehicle exhaust, and biomass burning sources. Elevated OC/EC ratios (8.0) during mid-December can be attributed to biomass burning and coal combustion. High OC/EC ratios (6.0–9.0) during the Chinese Spring Festival may be due to lower contributions from motor-vehicle exhaust and biomass burning during the holiday, and higher contributions from residential coal combustion.

3.4 Contributions to $PM_{2.5}$ and PM_{10} mass

Figure 4 shows a larger PM_{10} scatter than $PM_{2.5}$ in both seasons. Daily PM_{10} in winter varied by a factor of 5.7, ranging from 155 $\mu g\,m^{-3}$ (06 November 2003) to 885 $\mu g\,m^{-3}$ (14 December 2003), and averaging 450.6 $\mu g\,m^{-3}$. The average for fall was 261.9 $\mu g\,m^{-3}$. The $PM_{2.5}$ average was 140.1 $\mu g\,m^{-3}$ in fall and 258.7 $\mu g\,m^{-3}$ in winter. $PM_{2.5}$ accounted for 55.6% of the PM_{10} in fall, ranging between 44.3% and 77.4%. In winter, $PM_{2.5}$ accounted for 60.4% of the PM_{10}, with a wide range from 33.0% and 97.6%. Compare to Xi'an, the percentage of $PM_{2.5}$ in PM_{10} in other Chinese cities was: Shenzhen in 2001 — 73.3% (Cao et al., 2003); Zhuhai, 2001 — 70.8% (Cao et al., 2003); Chongqing, 1997 — 65.1% (Wei et al., 1999); Wuhan, 1997 — 60.5% (Wei et al., 1999); Xi'an, 2003 — 60.4%; Lanzhou, 1997 — 51.9% (Wei et al., 1999). In Xi'an, only five of the 17 PM_{10} sampling days in fall and none of the 36 sampling days in winter were in compliance with China's legislated Class 2 PM_{10} standard of 150 $\mu g\,m^{-3}$ (GB 3905-1996). The data depict extreme PM pollution in Xi'an despite the current substantial local government pollution control efforts.

As shown in Table 2, total carbonaceous aerosol (TCA=OC×1.6+EC) contributed 48.8% of $PM_{2.5}$ in fall and 45.9% in winter. The percentage of TCA in PM_{10} was lower than in $PM_{2.5}$, with an average of 34.5% in fall and 37.0% in winter. This may be due to higher contributions of geological matter in coarse particles. The material balance also confirmed that TCA is the dominant component of $PM_{2.5}$ (Li, 2004). As shown in the time series in Fig. 2, TCA% varied around the 45% level during the study and did not correlate with changes of $PM_{2.5}$ mass or OC/EC concentrations.

$PM_{2.5}$ OC accounted for 81.8% and 72.8% of PM_{10} OC during fall and winter, respectively, whereas $PM_{2.5}$ EC accounted for 75.0% and 59.6% of PM_{10} EC in fall and winter (Table 1). Less than 60% of PM_{10} EC resided in $PM_{2.5}$ in winter, possibly due to coarse soot particles in the emissions of incomplete coal combustion, or from fugitive coal dust.

3.5 The characterization of eight carbon fractions

The IMPROVE_TOR protocol does not advance from one temperature to the next until a well-defined carbon peak has evolved (Chow et al., 1993, 2004a). Carbon abundances in each of these fractions differ by carbon source (Chow et al., 2004b; Watson et al., 1994). Eight carbon fractions have

Table 2. Statistical summary of the percentage of OC, EC, and TCA% in $PM_{2.5}$ and PM_{10}^{a}.

Season	Month	TCA (%) $PM_{2.5}$	TCA (%) PM_{10}	TCA (%) $PM_{2.5}/PM_{10}$	OC (%) $PM_{2.5}$	OC (%) PM_{10}	OC (%) $PM_{2.5}/PM_{10}$	EC (%) $PM_{2.5}$	EC (%) PM_{10}	EC (%) $PM_{2.5}/PM_{10}$
Fall	September	45.0±7.6 [a]	26.4±1.5	83.0±6.4	23.5±4.3	13.6±1.0	84.9±5.8	7.3±1.6	4.7±0.8	74.8±13.4
	October	51.0±10.7	38.8±8.8	79.4±6.2	26.6±5.5	20.4±4.8	80.2±6.1	8.4±2.7	6.3±1.6	75.0±10.1
	Average	48.8±10.1	34.5±9.3	80.7±6.3	25.5±5.3	18.0±5.1	81.8±6.3	8.0±2.4	5.7±1.6	75.0±11.0
Winter	November	44.8±7.4	35.7±4.6	69.8±11.8	24.3±3.9	18.9±2.5	71.8±12.2	5.9±1.7	5.4±0.9	58.7±12.0
	December	50.3±5.5	42.4±7.7	65.9±13.3	27.9±2.8	23.0±4.5	67.6±14.0	5.6±1.5	5.6±1.3	55.2±10.6
	January	44.0±8.1	37.0±11.7	75.0±9.1	24.9±4.6	20.6±7.1	77.0±9.6	4.0±1.1	4.1±0.8	61.4±7.3
	February	44.8±7.5	32.4±7.4	72.2±11.9	24.2±4.4	17.2±4.3	74.0±13.1	6.1±1.4	4.9±0.8	63.2±9.4
	Average	45.9±7.5	37.0±8.9	71.0±11.5	25.4±4.2	20.0±5.3	72.8±12.1	5.4±1.6	5.0±1.1	59.6±9.8

[a] values represent average ± standard deviation

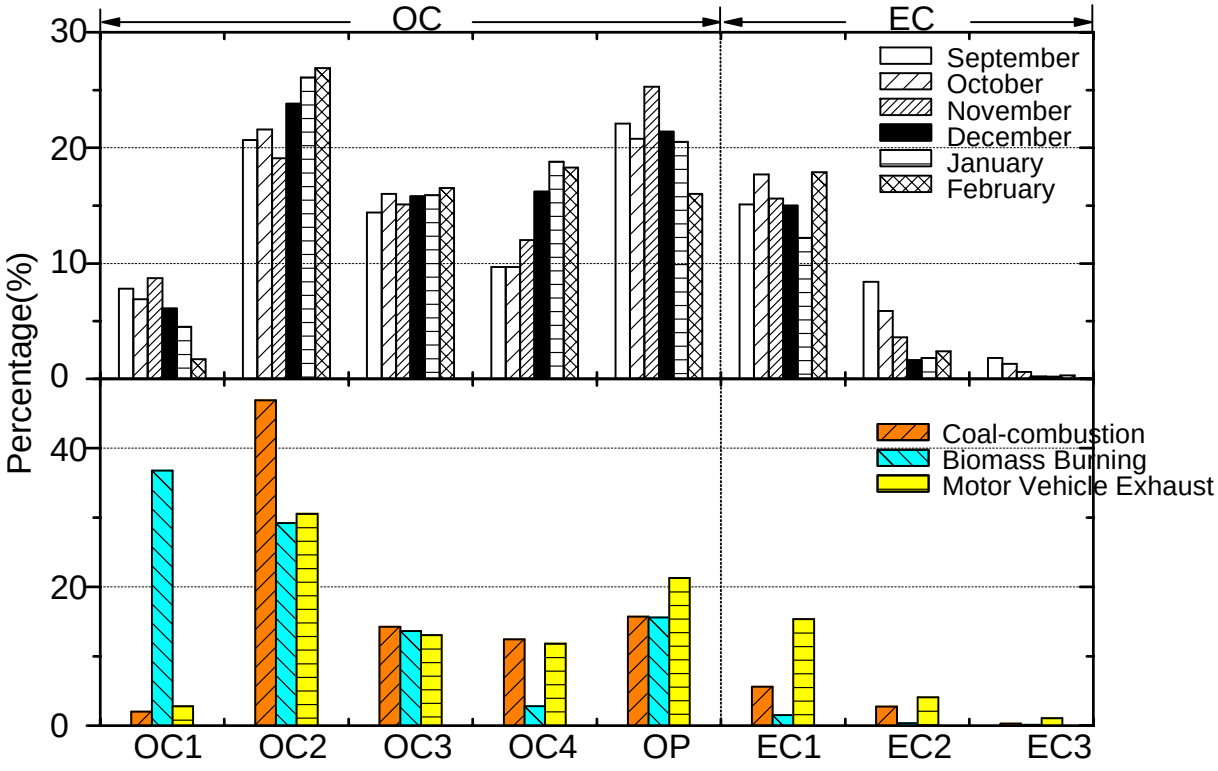

Fig. 5. Abundances (mass fraction of total carbon) of eight thermally-derived carbon fractions in ambient and source samples.

been used before for the source apportionment of carbonaceous aerosol (Kim et al., 2003a, b; Kim and Hopke, 2004).

The average percentages of eight carbon fractions in ambient and source samples are shown in Fig. 5. Distinct differences in carbon fractions are evident among samples from the three source types tested in this study. OC1 contributed 36.8% to TC in biomass-burning samples, 2.0% in coal-combustion samples, and 2.8% in motor-vehicle exhaust samples. OC2 accounted for 46.9% of TC in coal-combustion samples, 29.2% in biomass-burning samples and 30.5% in motor-vehicle samples. EC1 constituted 15.4% to TC, 5.6% in coal-combustion samples and 0.4% in biomass-burning samples.

Monthly variations of the eight carbon fractions were related to the contributions of different emission sources. November experienced the highest contribution from biomass burning, with OC1 attaining 8.7%, which was the highest value in the six months of the study. OC1 decreased to 1.7% in February. OC2 increased during the six months (except for November), possibly reflecting the increased contributions of coal combustion from fall to winter. EC1 reached its lowest values in January, possibly caused by

Table 3. Comparison of $PM_{2.5}$ OC, EC at Xi'an with other Asian cities.

City	Period	TC	OC ($\mu g\,m^{-3}$)	EC	OC/EC	Measurement method	Reference
Xi'an	Fall, 2003	45.4	34.1±18.0	11.3±6.9	3.3	IMPROVE_TOR	This study
	Winter 2003	74.2	61.9±33.2	12.3±5.3	5.1	IMPROVE_TOR	This study
Beijing[1]	Fall 1999	39.0	28.8	10.2	2.8	IMPROVE_TOR	He et al. (2001)
	Winter 1999	42.6	31.5	11.1	2.8	IMPROVE_TOR	
Beijing[2]	December 2002	51.9	36.7±19.4	15.2±11.1	3.5	Elemental analyzer	Dan et al. (2004)
Beijing[3]	November 1997–October 1998		41.5 [4]	No data		Elemental analyzer	Duan et al. (2004)
Shanghai[5]	Fall 1999	23.2	16.3	6.9	2.4	IMPROVE_TOR	Ye et al. (2003)
	Winter, 1999	25.1	17.0	8.1	2.1	IMPROVE_TOR	
Hong Kong	January–February 2002	14.4	9.6±4.5	4.7±2.9	2.3	IMPROVE_TOR	Cao et al. (2003)
Guangzhou	January–February 2002	31.0	22.6±18.0	8.3±5.6	2.7	IMPROVE_TOR	Cao et al. (2003)
Shenzhen	January–February 2002	19.2	13.2±4.1	6.1±1.8	2.2	IMPROVE_TOR	Cao et al. (2003)
Zhuhai	January–February 2002	17.3	12.2±4.4	5.0±1.6	2.4	IMPROVE_TOR	Cao et al. (2003)
Kaohsiung	November 1998–April 1999	14.5	10.4	4.0	2.6	Elemental analyzer	(Lin & Tai, 2001)
Chongju, Korea	Fall, 1995	12.4	6.0	6.4	0.9	IMPROVE_TOR	Lee and Kang (2001)
	Winter 1995	9.3	5.0	4.3	1.2	IMPROVE_TOR	
Sapporo, Japan	September–October 1992	9.1	4.1	5.0	0.8	Elemental analyzer	Ohta et al. (1998)
	January–February 1992	9.0	3.9	5.1	0.8	Elemental analyzer	
Uji, Japan	September–October 1998	6.4	1.8	4.6	0.4	R&P 5400	Holler et al. (2002)
	November–December 1998	10.2	2.5	7.7	0.3	R&P 5400	

[1] Chegongzhuang site.
[2] Average of 3 sites: Beijing Normal University, Capital Steel Plant, Yihai Garden.
[3] Temple of Heaven.
[4] Annual average.
[5] Average of Tongji University and Hainan Road.

lower motor vehicle activity during the Chinese Spring Festival. OP ranged from 16.0% to 22.1%, with an average of 21.0%. These ratios are higher than the 8.0 to 17.8% OP in TC found during summer for the Pearl River Delta Region in China (Cao et al., 2004).

3.6 Periodic characteristics of OC and EC

The periodic features of emission sources and meteorological conditions can be identified from the OC/EC time series. Hies (2000) showed that domestic heating by coal combustion appears with a 365-day periodicity. In this study, traffic in Berlin, Germany contributes 3.5-, 4.6-, and 7-day peaks in the spectrum, and periodicity for elevated EC can be identified in the 13- to 42-day range.

The comparison of periodicities of OC, EC, $PM_{2.5}$ mass, and daily average wind speed are illustrated in Fig. 6. These curves were obtained by AutoSignal 1.0 software (SPSS, USA). The common periodicities of OC, EC and $PM_{2.5}$ were 24, 10, 7, and 5 days. Identical periodicities between $PM_{2.5}$ mass and OC are consistent as they are controlled by similar processes. In agreement with Hies (2000), the periodicities of motor vehicle variations were five and seven days. Precipitation events had 10-day periodicity from September to November. This periodicity should reflect the impact of precipitation on OC and EC concentrations. Thirteen-day periodicity was a major component in the wind speed spectrum identified by Hies (2000), which also influences EC concentrations. Sixty-day peaks may be related to the change of primary emission sources.

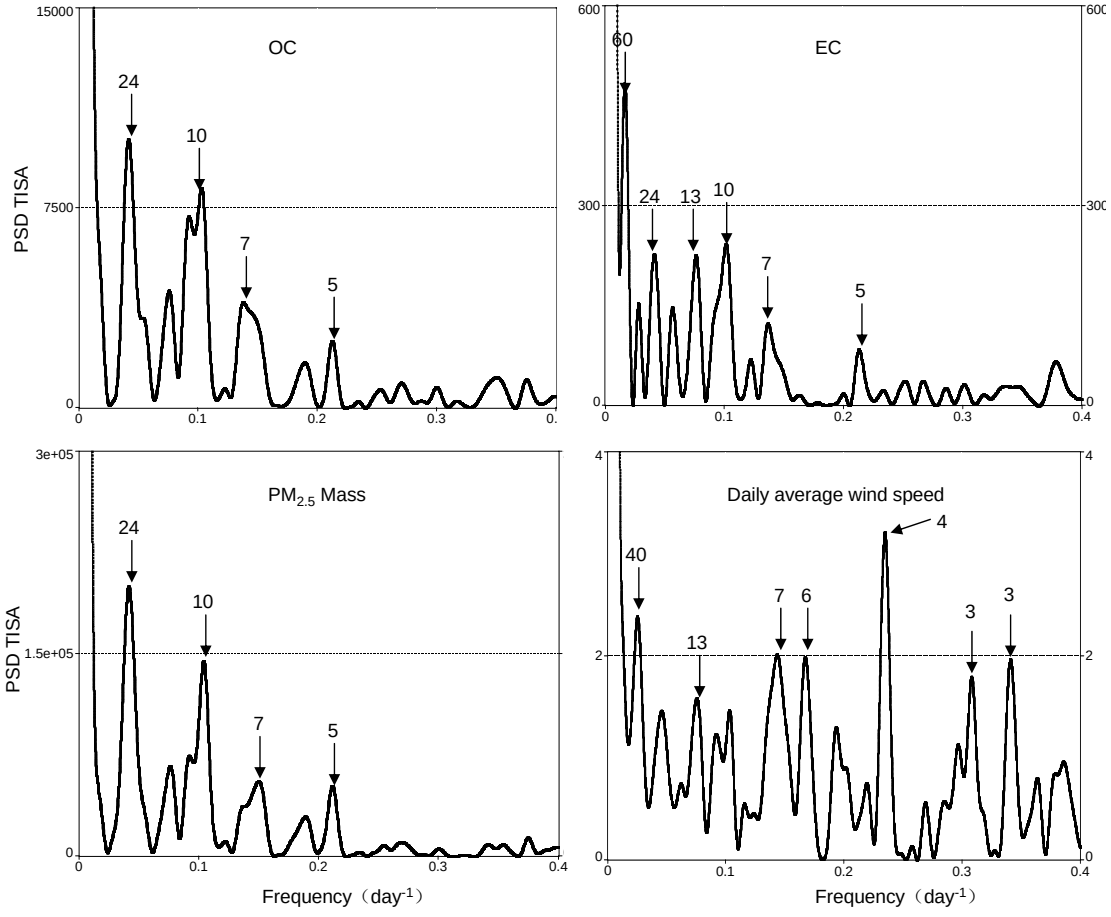

Fig. 6. Periodicity of $PM_{2.5}$ OC, EC, mass, and daily average wind speed. (PSD TISA on the Y axis refers to Power as Time-Integral Squared Amplitude.)

3.7 Comparison of OC and EC with other Asian cities

Table 3 compares TC, OC, and EC concentrations in $PM_{2.5}$ from 11 Asian cities. Total carbon in fall and winter at Xi'an ranked the highest. While OC and EC concentrations were similar in Beijing and Xi'an in fall, OC in Xi'an was twice that of Beijing in winter, with similar EC levels. This may be due to more motor vehicles and less coal use in Beijing (Yang et al., 2005). Winter OC levels in Xi'an were 2.7, 3.6, 4.7, 5.1, and 6.4 times those in Guangzhou, Shanghai, Shenzhen, Zhuhai, and Hong Kong, respectively (the number of motor vehicles in these coastal cities are 1.1, 0.7, 0.7, 0.3, and 0.5 million, respectively, compared with 0.2 million in Xi'an). Winter EC levels in Xi'an were 1.5, 1.5, 2.0, 2.5, and 2.6 times those of these coastal cities. The lower increment for EC may be attributed to the high emissions of motor-vehicle exhaust in the coastal cities, and the larger increment for OC may be ascribed to the lower use of coal for residential heating (there is almost no use of coal for residential heating in the coastal cities). Winter OC and EC levels in Xi'an were 12.4 and 2.9 times, respectively, those in Chongju, South Korea (Lee and Kang, 2001).

3.8 Source apportionment of carbonaceous PM

Absolute principal component analysis (APCA) (Thurston and Spengler, 1985) was applied to the eight carbon fraction concentrations to identify and quantify source contributions. The first step in APCA is the normalization of all carbon concentrations as Z_{ik}. This is done by adding a zero concentration sample as case 0 (The Z_{i0} is obtained by deriving the Z-score for absolute zero concentrations).

$$Z_{ik} = (C_{ik} - C_i)/S_i \quad (1)$$

where C_{ik} is the concentration of carbon fraction i in sample k, C_i is the arithmetic mean concentration of carbon fraction i, and S_i is the standard deviation of carbon fraction i for all samples included in the analysis. The normalization process allows any continuous variable, such as wind speed, to be included in future analyses along with the carbon data.

Regressing the TC data on these absolute principal component scores (APCS) gives estimates of the coefficients which convert the APCS into TC contributions from each source for each sample. For each source identified by the APCA,

Table 4. APCA results of fall samples.

	F1	F2	F3
OC1	0.32	0.12	0.91
OC2	0.96	0.16	0.17
OC3	0.89	0.11	0.38
OC4	0.95	0.19	0.19
OP	0.88	0.25	0.13
EC1	0.88	0.21	0.39
EC2	0.62	0.65	−0.28
EC3	0.12	0.94	0.23
Variance	68%	14%	10%
Eigen value	5.60	1.10	0.80
	Gasoline Exhaust	Diesel Exhaust	Biomass Burning

Table 5. APCA results of winter samples.

	F1	F2	F3
OC1	0.09	0.98	0.06
OC2	0.97	0.03	0.05
OC3	0.87	0.44	0.07
OC4	0.96	0.05	−0.01
OP	0.60	0.67	0.24
EC1	0.73	0.50	0.17
EC2	−0.05	0.12	0.90
EC3	0.17	0.06	0.88
Variance	55%	21%	13%
Eigen value	4.40	1.60	1.10
	Coal Combustion + Gasoline Exhaust	Biomass Burning	Diesel Exhaust

the weighted regression of each carbon fraction's concentration on the predicted TC contributions yields estimates of the content of that fraction in each source, as follows:

$$C_{ik} = b + \sum_{j=1}^{n} a_{ij} M_{jk} \quad (2)$$

where C_{ik} is the concentration of carbon fraction i in sample k; b is a constant; a_{ij} is the mean TC fraction of source j's particles represented by carbon fraction i, and M_{jk} is the TC concentration of source j for observation k. By repeating this weighted least-square regression for each of the i=1, 2,...n carbon fractions considered in this analysis, one can estimate the mean concentration of the carbon fractions for each factor.

Results for fall and winter are summarized in Tables 4 and 5. Factor 1 (F1) in fall was highly loaded with OC2, OC3, OC4, OP, and EC1. This factor appears to represent gasoline-motor-vehicle exhaust (Chow et al., 2004b). Factor 2 (F2) was highly loaded with high-temperature EC2 and EC3 and appears to represent diesel-vehicle exhaust (Watson et al., 1994). The high loading of OC1 in factor 3 (F3) reflects the contribution of biomass burning. In winter, the highly loaded OC2, OC3, OC4, and EC1 in F1 might represent the mixture of coal-combustion and motor-vehicle exhaust. Similar to the fall results, F2 and F3 in winter represent biomass burning and diesel-vehicle exhaust, respectively.

To simplify the estimation, it is assumed that there is no contribution of coal combustion in fall, and there are equal contributions from gasoline-powered motor vehicles in fall and winter. Coal combustion in winter is assumed to be the difference between winter F1 and fall F1, thus the source attributions can be resolved for the two seasons (Fig. 7). During fall, TC is composed of 73% from gasoline exhaust, 23% from diesel exhaust, and 4% from biomass burning. During winter, TC receives 44% from gasoline exhaust, 3% from diesel exhaust, 9% from biomass burning, and 44% from coal burning.

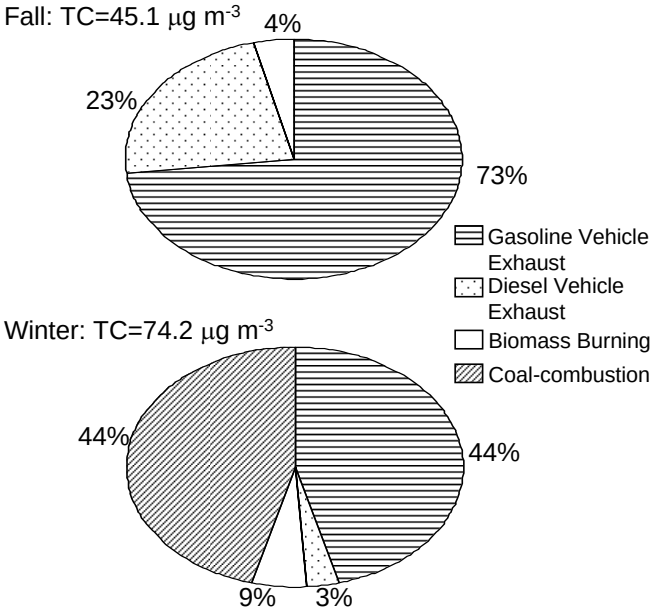

Fig. 7. Relative contributions of major sources to $PM_{2.5}$ TC during fall and winter 2003.

4 Conclusions

Six months of continuous observations were conducted at Xi'an, Shaanxi Province, China to gain insight into the characterization and source apportionment of organic and elemental carbon (OC/EC). Major findings are as follows.

1. Average $PM_{2.5}$ OC concentrations during fall and winter were $34.1\pm18.0\,\mu g\,m^{-3}$ and $61.9\pm33.2\,\mu g\,m^{-3}$; EC concentrations were $11.3\pm6.9\,\mu g\,m^{-3}$ and

$12.3\pm5.3\,\mu g\,m^{-3}$, respectively. Carbonaceous aerosol accounted for 48.8±10.1% and 45.9±7.5% of $PM_{2.5}$ and 34.5±9.3% and 37± 8.9% of PM_{10} during fall and winter, respectively. This indicates that carbonaceous aerosol is the dominant component of fine particles in Xi'an.

2. All of the OC/EC ratios exceeded 2.0, and average OC/EC ratios were 3.3 in fall and 5.1 in winter. Elevated OC/EC ratios were found during heating seasons with increased primary emissions, such as residential coal combustion. $PM_{2.5}$ OC and PM_{10} OC were highly correlated (R=0.95–0.97) during fall, and moderately correlated (R=0.81) during winter.

3. $PM_{2.5}$ total carbon source apportionment by APCA attributed 73% to gasoline engine exhaust, 23% to diesel engine exhaust, and 4% to biomass burning during fall, and 44% to gasoline engine exhaust, 44% to residential coal burning, 9% to biomass burning, and 3% to diesel engine exhaust during winter. Motor-vehicle exhaust and coal combustion were the dominant sources for carbonaceous aerosol in Xi'an.

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