



## Carbonaceous aerosols in PM<sub>10</sub> and pollution gases in winter in Beijing

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### Abstract

An intensive observation of organic carbon (OC) and elemental carbon (EC) in PM<sub>10</sub> and gaseous materials (SO<sub>2</sub>, CO, and O<sub>3</sub>) was conducted continuously to assess the characteristics of wintertime carbonaceous aerosols in an urban area of Beijing, China. Results showed that the averaged total carbon (TC) and PM<sub>10</sub> concentrations in observation period are  $30.2 \pm 120.4$  and  $172.6 \pm 198.3$   $\mu\text{g}/\text{m}^3$ , respectively. Average OC concentration in nighttime ( $24.9 \pm 19.6$   $\mu\text{g}/\text{m}^3$ ) was 40% higher than that in daytime ( $17.7 \pm 10.9$   $\mu\text{g}/\text{m}^3$ ). Average EC concentrations in daytime ( $8.8 \pm 15.2$   $\mu\text{g}/\text{m}^3$ ) was close to that in nighttime ( $8.9 \pm 15.1$   $\mu\text{g}/\text{m}^3$ ). The OC/EC ratios in nighttime ranging from 2.4 to 2.7 are higher than that in daytime ranging from 1.9 to 2.0. The concentrations of OC, EC, PM<sub>10</sub> were low with strong winds and high with weak winds. The OC and EC were well correlated with PM<sub>10</sub>, CO and SO<sub>2</sub>, which implies they have similar sources. OC and EC were not well correlated with O<sub>3</sub>. By considering variation of OC/EC ratios in daytime and night time, correlations between OC and O<sub>3</sub>, and meteorological condition, we speculated that OC and EC in Beijing PM<sub>10</sub> were emitted as the primary particulate form. Emission of motor vehicle with low OC/EC ratio and coal combustion sources with high OC/EC ratio are probably the dominant sources for carbonaceous aerosols in Beijing in winter. A simple ratio method was used to estimate the relative contribution of sources to carbonaceous aerosols in Beijing PM<sub>10</sub>. Motor vehicle source accounts for 80% and 68%, while coal combustion accounts for 20% and 32% in daytime and nighttime, respectively in Beijing. Averagely, the motor vehicle and coal combustion accounted for 74% and 26%, respectively, for carbonaceous aerosols during the observation period. It points to the motor vehicle is dominant emission for carbonaceous aerosols in Beijing PM<sub>10</sub> in winter period, which should be paid attention to control high level of PM<sub>10</sub> in Beijing effectively.

**Key words:** organic carbon; elemental carbon; diurnal variation; PM<sub>10</sub>

### Introduction

Atmospheric carbonaceous aerosols comprise significant fraction of ambient respirable suspended particulates (PM<sub>10</sub>) ranging from approximately 10% in remote areas to approximately 40% in urban areas and industrialized areas (Seinfeld and Pandis, 1998). Carbonaceous aerosols play an important role in the atmosphere with regard to radiative transfer, health effects, and atmospheric chemistry (Höller *et al.*, 2002; Watson, 2002; Bond *et al.*, 2004). They are generally divided into organic carbon (OC) and elemental carbon (EC) (also called black carbon, BC). OC containing polycyclic aromatic hydrocarbon and other components with possible mutagenic and carcinogenic effects, can be directly emitted from sources (primary

OC) or produced from atmospheric reactions involving gaseous organic precursors (secondary OC, SOC) (Turpin and Huntzicker, 1995; Molnár *et al.*, 1999). Recently, EC is of special interest due to its warm effect on climate (Zhang *et al.*, 2005a). EC is regarded to be the second most important component of global warming in terms of direct forcing, after CO<sub>2</sub> (Jacobson, 2001). Simulation study by Menon *et al.* (2002) implies that EC emissions from China and India may be responsible for the increase in droughts in North China and flooding in South China in the summer observed during the last 20 years. Due to the importance of OC and EC on climate and atmospheric chemistry, information concerning the concentrations and distributions of carbonaceous aerosol in atmosphere is of great interest (Zhang, 2004).

Beijing, one of the biggest cities in the world, also the capital of China, has 14 million populations and 2.1 million motor vehicles by the end of 2003. Due to increased economic activities and the number of vehicles and urbanization, high particulate matter pollution and poor visibility have become a serious problem in Beijing.

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From 1999, the municipal government undertook several powerful control measures to reduce particle pollution for the Olympic Game to be held in Beijing in 2008. The air quality has improved since 1999. The mass concentrations of PM<sub>10</sub>, however, are still at high levels. According to the Environmental Annual Report from Beijing Environmental Protection Bureau, from 1999 to 2001, the annual average concentration of TSP in atmosphere over Beijing is 364, 353, and 370  $\mu\text{g}/\text{m}^3$ , respectively; and that of PM<sub>10</sub> is 180, 162 and 165  $\mu\text{g}/\text{m}^3$ , respectively (Liu *et al.*, 2004). As a consequence, an investigation of atmospheric carbon pollution in the Beijing is important, as it is a major component of particulate pollutions. In recent years, many studies have been performed in the world focusing on the carbonaceous aerosols (Turpin *et al.*, 2000; Chow *et al.*, 2004; Novakov *et al.*, 2005). However, there were limited studies on the OC/EC in Asia, with fewer focused on OC and EC in China. To date several studies on carbonaceous particles in PM<sub>10</sub> in China were reported (Cao *et al.*, 2003, 2004, 2005; Yu *et al.*, 2004), but few studies concentrated on continuous observation of OC and EC (Duan *et al.*, 2005; Wang *et al.*, 2005).

In this work, we measured carbonaceous aerosol in PM<sub>10</sub> continuously in winter period because (1) China Environment Protection Administration (China EPA) adopts PM<sub>10</sub> air pollution standard; (2) winter is the worst pollution season in Beijing and is of the most concern; (3) till now, there is no report about the relationship between carbonaceous aerosols and pollution gases. Continuous concentration of PM<sub>10</sub> and pollution gases of CO, SO<sub>2</sub>, and O<sub>3</sub> are also monitored simultaneously. The objective of this paper is to present the diurnal variation of OC/EC and their fraction in PM<sub>10</sub> in Beijing and their relation to pollution gases in Beijing.

## 1 Methodology

### 1.1 Observation site

Measurements of carbonaceous aerosol and gases were performed at the Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences (CAS), which lies between the North Third Ring Road and the North Fourth Ring Road in Beijing (39°58'N, 116°22'E). This location is a typical urban area. The instrumentation used in this work was setup on the roof of two-storey (10 m above ground) of a building of IAP/CAS. A 325-m high meteorological tower, 50 m to the north of this observation site, provides wind speed and wind direction. This site was a super observation site of ACE-Asia for aerosol and dust storm research (Zhang *et al.*, 2005b).

### 1.2 Experiment

#### 1.2.1 PM<sub>10</sub> mass concentration

The tapered element oscillating microbalance (TEOM) 1400a series, manufactured by Rupprecht and Patashnick Co. Inc., was used for the continuous measurement of PM<sub>10</sub> mass concentration. It is a US EPA equivalent method providing PM<sub>10</sub> masses from a 16.7 L/min air flow

(Salter and Parsons, 1999). It has a high accuracy with  $\pm 1.5 \mu\text{g}/\text{m}^3$  and high resolution with  $0.1 \mu\text{g}/\text{m}^3$ . However, TEOM records slightly lower concentration values than those determined by reference samplers. The TEOM is widely used in different aerosol studies (King, 2000; Höller *et al.*, 2002; Kuhlbusch *et al.*, 2001; Even *et al.*, 2000).

#### 1.2.2 Continuous observation of organic and element concentrations

The concentrations of particulate OC and EC were continuously detected by a thermal analysis method using ambient carbon particulate monitors, Model 5400 manufactured by Rupprecht and Patashnick Co. Inc. This instrument performs a thermal evolution analysis of carbonaceous material (Höller *et al.*, 2002; Long *et al.*, 2003). Sampling interval was set at 3-h here. The sample is collected on impactors instead of filters to reduce positive artifacts due to adsorption of organic vapor. Analysis of the samples is performed in a closed cycle, which includes the impactor, a NDIR CO<sub>2</sub> sensor, and an afterburner, which heats the gas stream to 750°C to burn all remaining material. The amounts of carbonaceous substances evolved at 280, 340°C were defined as organic carbon (OC) and 750°C as total carbon (TC). And then, the difference between the amounts of TC and OC gives the amount of EC. Comparison between the Aethalometer and the R&P 5400 ambient carbon particulate monitor (Artaxo *et al.*, 1999) shows good agreement and both instruments give confidence in the measurement of the black carbon concentration for urban areas. More detailed description of this instrument has been given in the previous studies (Höller *et al.*, 2002; Matsumoto *et al.*, 2003a, b; Castanho and Artaxo, 2001). R&P 5400 has a high resolution of  $0.25 \mu\text{g}/\text{m}^3$ . The R&P 5400 is calibrated by Beijing Branch of Rupprecht & Patashnick Co. Inc. before observation. The thermal method used by the R&P 5400 is one of the major techniques for carbonaceous aerosols measurements (Cachier *et al.*, 1989). But, it faced negative artifact problems, which were caused both by the missing collection of particles smaller than  $0.14 \mu\text{m}$  and by the evaporation of the organic gases (Matsumoto *et al.*, 2003a, b), and this problem still need to be resolved.

#### 1.2.3 Ozone (O<sub>3</sub>), carbon monoxide (CO), and sulfur dioxide (SO<sub>2</sub>)

O<sub>3</sub> was monitored using a commercial UV photometric instrument (Thermo-Environmental Instruments, Inc. TEI), Model 49C, which had a detection limit of 1 ppbv and a precision of 1 ppbv for a 1-min average. CO was measured with an infrared gas filter correlation analyzer (TEI, Model 48C). The detection limit was estimated to be 40 ppbv for a 1-min integration time, and the precision was approximately 40 ppbv. SO<sub>2</sub> was detected by using a pulsed UV fluorescence analyzer (TEI, Model 43S). The detection limit for this analyzer is 0.06 ppbv with a precision of about 0.2 ppbv. More details about above gases instrument has been given in previous studies on air pollution in Beijing (Liu *et al.*, 1999; Chen *et al.*, 2000).

Calibration of for monitoring O<sub>3</sub>, CO, and SO<sub>2</sub> were

conducted before observation. Calibration of  $O_3$  (49C) was performed before and controlled after the campaign with a Thermo-Environmental Instrument 49PS model for ozone. Calibration of  $CO$  (48C model) was performed with calibrated gases from National Standard Material Center of China. Calibration of  $SO_2$  (43S model) was performed with calibration gas cylinders from National Standard Material Center of China. The data of  $PM_{10}$ , OC, EC,  $SO_2$ ,  $CO$ ,  $O_3$  and wind are obtained in observation period during 1–15 January 2004 by using above instruments. As sampling interval was set at 3-h for R&P 5400, the  $PM_{10}$ , 1-min interval data of  $O_3$ ,  $CO$  and  $SO_2$  are averaged in the same periods as OC and EC.

## 2 Results and discussion

### 2.1 Diurnal variations of concentrations of organic carbon and elemental carbon

Fig.1 compares the temporal variations of OC, EC,  $PM_{10}$  concentration, TC/ $PM_{10}$ , OC/EC, wind speed and direction (at the height of 102 m),  $SO_2$ ,  $CO$ , and  $O_3$  during 1–15 January 2004. There is no notable precipitation recorded in observation period. The  $PM_{10}$  concentration in observation period varied between 24.2–401.6  $\mu g/m^3$  with averaged value of  $172.6 \pm 98.3 \mu g/m^3$ , which has exceeded 100  $\mu g/m^3$ , the Second Annual Ambient Air Quality Standard of  $PM_{10}$  by China Environmental Protection Administration. It means that the  $PM_{10}$  pollution in Beijing is still serious. The OC in  $PM_{10}$  varied between 3.0–72.3  $\mu g/m^3$  with averaged value of  $21.2 \pm 16.0 \mu g/m^3$ . The EC concentration in  $PM_{10}$  varied between 1.7–20.1  $\mu g/m^3$  with averaged value of  $8.9 \pm 5.1 \mu g/m^3$ . OC/EC ratio varied from 1.2 to 5.7 with averaged value of 2.3. The OC, EC and TC account for  $(12.4 \pm 6.4)\%$ ,  $(5.6 \pm 2.3)\%$  and  $(18 \pm 9.2)\%$  to  $PM_{10}$  mass respectively.

However, the concentrations of OC, EC,  $PM_{10}$  and

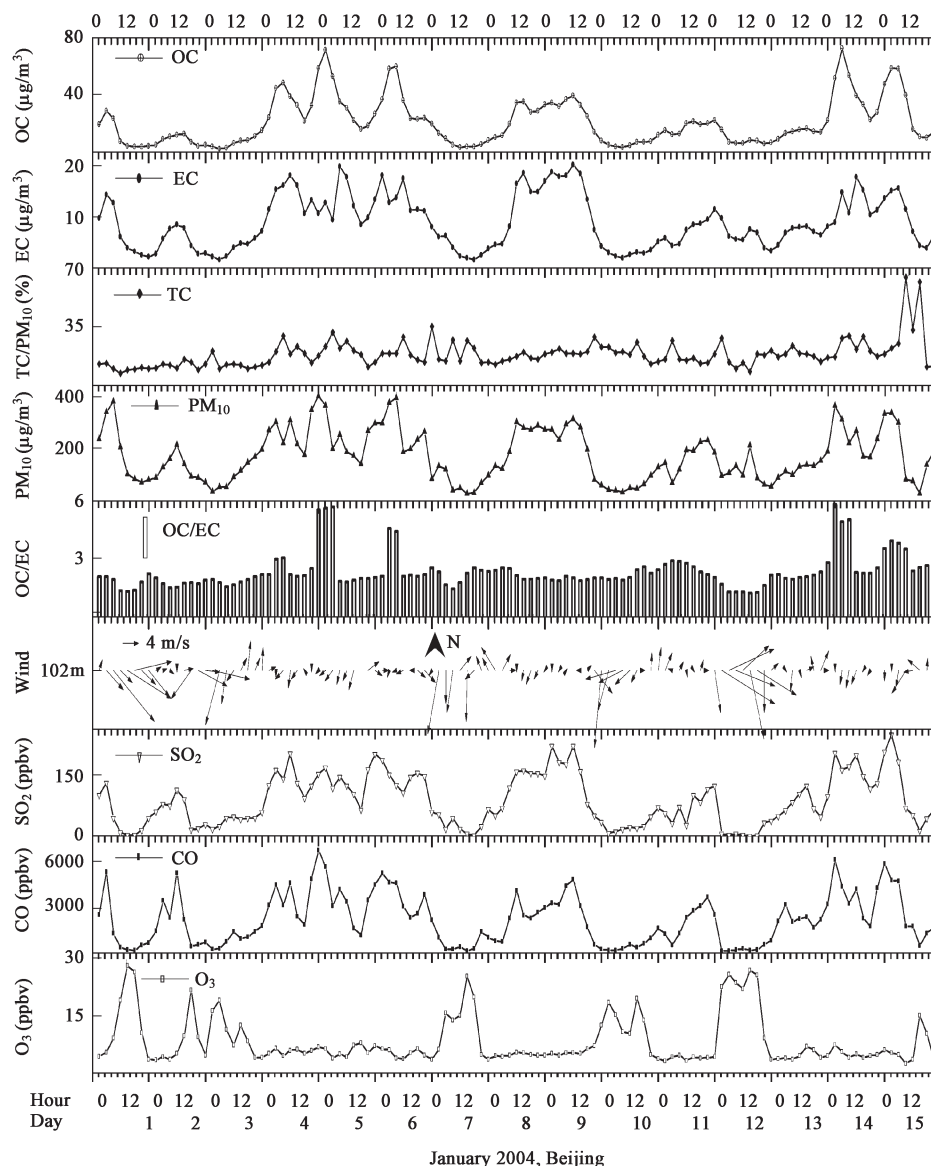


Fig. 1 Time series of surface OC, EC, TC/ $PM_{10}$ ,  $PM_{10}$ , OC/EC, wind,  $SO_2$ ,  $CO$ , and  $O_3$  in January 2004 in Beijing. TC=OC+EC, wind is at the height of 102 m.

OC/EC ratio varied significantly in different day as they are influenced greatly by meteorological condition and emissions. Dynamical processes and meteorological conditions may cause perturbations in the boundary layer and can influence atmospheric trace constituent concentrations (Bhugwant and Bremaud, 2001). The concentrations of OC, EC, PM<sub>10</sub> reach low values on 1, 2, 3, 7, 10, 12, 15 January 2004 when the correspondence wind is strong. The wind strength can be associated to the "cleaning effect" of the air at observation site through the dispersion of particles and trace gases. This can explain the above low concentration of particles matters. OC/EC ratios reach minimum of approximately 1.2 in the afternoon on 1 January and 1:30–16:30 on 12 January 2004 in strong wind period. The concentrations of OC, EC, PM<sub>10</sub> reach the high when the wind is weak. When wind speed is low, the atmosphere is often stable and slow dispersion occurred. The emitted pollutants will be easily accumulated, resulting with high concentration of PM. The variations of SO<sub>2</sub> and CO are similar to that of OC, EC and PM<sub>10</sub> as they are mainly emitted from the ground sources. O<sub>3</sub> concentration is low when wind is not strong and reaches peak value when strong wind occurs.

Table 1 presents the diurnal variations of OC, EC, PM<sub>10</sub> and OC/EC ratio, TC/PM<sub>10</sub> ratio at Beijing in January 2004. The PM<sub>10</sub> concentrations in nighttime are obviously higher than that in daytime. The boundary layer usually becomes deeper in daytime because of stronger turbulent eddies (Zhang *et al.*, 2002). This dilutes particle pollutions released at the surface and results in lower ambient concentration. Average OC concentrations are 17.7±10.9 µg/m<sup>3</sup> in daytime and 24.9±19.6 µg/m<sup>3</sup> in nighttime, respectively. OC concentrations are obviously higher in nighttime than in daytime and have peak value in midnight due to accumulation of emission in stable atmosphere. Averaged EC concentrations in daytime (8.8±5.2 µg/m<sup>3</sup>) are close to that in night time (8.9±5.1 µg/m<sup>3</sup>). For EC, a distinct morning peak clearly corresponds to the morning traffic rush hour. The OC/EC ratios in nighttime ranging

from 2.4 to 2.7 were higher than that in daytime ranging from 1.9 to 2.0.

Table 2 gives the comparisons of several studies by using R&P 5400 instrument for PM<sub>2.5</sub> carbonaceous aerosol in winter period. PM<sub>2.5</sub> constitutes 64% of PM<sub>10</sub> mass in Beijing (He *et al.*, 2001). Although PM<sub>10</sub> is determined in this study and PM<sub>2.5</sub> is observed in others study, the TC concentration in Beijing is still higher than that in USA and Japan. Prior study by He *et al.* (2001) also reported high level of the carbonaceous aerosol loading in PM<sub>2.5</sub> in winter. The OC/EC ratios between PM<sub>10</sub> and PM<sub>2.5</sub> (He *et al.*, 2001) were similar in Beijing (2.3 for PM<sub>10</sub> and 2.7 for PM<sub>2.5</sub>); and such value was very closely to that in Brazil, but much higher than that in Japan and USA. The results implied that the sources of OC and EC in Beijing might be different from that in USA and Japan but similar with that in Brazil.

## 2.2 Relationship of organic carbon and elemental carbon

The sources of carbonaceous aerosols can be qualitatively estimated by studying the relationship between OC and EC concentrations (Turpin and Huntzicker, 1995). If major fractions of OC and EC are emitted by a dominant primary source (e.g., vehicle emissions, coal combustion), the correlation between the OC and EC concentrations should be high because the relative rates of OC and EC emission would be proportional to each other. The regression between the OC and EC concentrations in PM<sub>10</sub> samples during winter in Beijing is given in Fig.2. There is an excellent correlation between OC and EC in daytime ( $R^2=0.94$ ) which implies that motor vehicles exhaust is probably the dominant sources in daytime. There is a relatively weaker correlation between OC and EC in nighttime ( $R^2=0.58$ ), which suggests that OC and EC fractions in Beijing PM<sub>10</sub> may not be released from a single, dominant primary source. The reason for this difference may be explained by the impact of other sources besides local vehicular emissions (i.e., secondary OC or

**Table 1 Diurnal variation of concentration of OC, EC, PM<sub>10</sub> and ratio of OC/EC, TC/PM<sub>10</sub> at Beijing in January 2004**

	Local time	OC (µg/m <sup>3</sup> )	EC (µg/m <sup>3</sup> )	OC/EC average	TC (µg/m <sup>3</sup> )	PM <sub>10</sub> (µg/m <sup>3</sup> )	TC/PM <sub>10</sub> (%)
Day	9 (07:30–10:30)	21.2±13.5	10.6±6.2	1.9±0.4	31.8±19.6	177.3±91.4	18.1±6.8
	12 (10:30–13:30)	18.7±10.9	9.5±5.4	2.0±0.4	28.2±16.2	153.1±79.1	21.3±12.3
	15 (13:30–16:30)	15.1±7.9	7.6±3.9	2.0±0.4	22.6±11.7	144.2±66.2	15.8±3.9
	18 (16:30–19:30)	16.0±9.1	7.5±3.9	2.1±0.3	23.5±12.9	173.6±92.5	13.9±4.5
Night	21 (19:30–22:30)	20.8±15.1	7.9±4.3	2.5±0.9	28.7±18.7	172.2±106.7	17.1±5.9
	0 (22:30–01:30)	25.4±20.2	8.9±5.2	2.7±1.3	34.3±24.2	192.7±114.8	17.7±4.8
	3 (01:30–04:30)	28.1±22.6	9.3±5.2	2.7±1.3	37.4±26.9	186.3±111.1	19.0±6.3
	6 (04:30–07:30)	25.2±18.5	9.7±5.4	2.4±1.1	34.9±22.9	176.9±113.1	21.7±13.1
Average		21.2±16.0	8.9±5.1	2.3±0.9	30.2±20.4	172.6±98.3	18.0±9.2

Values represent average standard deviation; TC=OC+EC.

**Table 2 Comparison of recent studies in winter period by R&P 5400**

Location	Winter sampling period	TC (µg/m <sup>3</sup> )	OC (µg/m <sup>3</sup> )	EC (µg/m <sup>3</sup> )	OC/EC	PM	Reference
Beijing, China	2004.01	30.2	21.2	8.9	2.3	PM <sub>10</sub>	This study
Uji, Japan	1998.12	6.23	2.57	3.66	0.7	PM <sub>2.5</sub>	Höller <i>et al.</i> , 2002
	1999.02	4.5	1.96	2.54	0.8	PM <sub>2.5</sub>	Höller <i>et al.</i> , 2002
Sao Paulo, Brazil	1997.07–09	23.4	15.8	7.6	2.1	PM <sub>2.5</sub>	Castanho and Artaxo, 2001
Salt Lake City, USA	1999–2000 winter	18.7	10.8	7.9	1.4	PM <sub>2.5</sub>	Long <i>et al.</i> , 2003

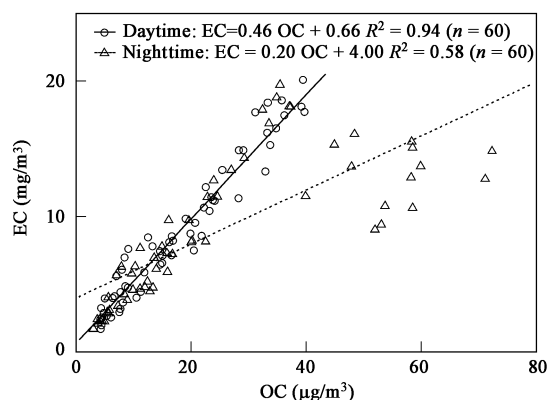


Fig. 2 Relationship between OC and EC concentration in PM<sub>10</sub> samples during winter in Beijing.

coal combustions).

Among 60 values in nighttime, OC and EC concentrations of 46 values are close to the regression line from daytime data (Fig.2), which implies that OC, EC may have similar and main sources (i.e. vehicles exhaust) in both daytime and nighttime. Also there exist discrete data in 14 values, which have high OC concentrations ranging from 44.5–72.3 µg/m<sup>3</sup> occurred at midnight with moderate EC concentrations ranging from 9.0–16.1 µg/m<sup>3</sup>. The high OC value resulted in high OC/EC ratio. This implies that other sources besides vehicles exhaust source exist in nighttime.

Diurnal differences in OC and EC concentrations were tested by the one-way analysis of variance (ANOVA) method, using the statistical software package SPSS v 11.0, and the results are shown in Table 3. OC has significant ( $p < 0.05$ ) diurnal variability, and EC was not statistically different. It means that OC has different sources in daytime and night time, which is consistent with previous description.

Table 3 One-way analysis of variance (ANOVA) for OC and EC on diurnal variables

OC		EC	
F-ratio	p-Value	F-ratio	p-Value
6.51	0.01	0.03	0.87

EC is essentially emitted as a primary pollutant; OC may derive from emitted particles (primary OC) as well as particles that are formed from gaseous precursors (secondary OC, SOC). Pandis' study (2002) indicated that the formation of secondary organic aerosol (SOA) in the ambient air was mainly controlled by temperature. The temperature at Beijing ranged from –6°C to 9°C with short duration of sunshine in observation period. It is not favorable meteorological conditions for the gas-particle conversion of gaseous hydrocarbon precursors to produce SOC. So the formation of SOA in Beijing may be low. Research by Cabada *et al.* (2002) showed that the corresponding contributions of SOC to the total organic PM concentration were nearly zero in winter in Pittsburgh, USA. Cao's study (2005) also showed that there was almost no SOC at Xi'an during winter. Study by Ma *et al.* (2004) indicated that a

large amount of the organic compounds was emitted as the primary particulate form from various combustion sources in heavily industrialized Kansai region in Japan in winter.

Watson *et al.* (2001) reported that OC/EC ratio is 1.1 from motor vehicle and 2.7 from coal combustion. Recent research by Cao *et al.* (2005) showed that OC/EC ratio from coal combustion is 12. These studies show that the OC/EC ratio is high in particles emitted from coal combustion and low from motor vehicle exhaust. As shown in Table 1, the minimum value of the OC/EC ratio occurs in the morning, coincident with the time of traffic peak. This is an evidence of the higher influence of direct vehicle emissions with relative low OC/EC ratio. During the nighttime, OC/EC ratios are relatively high. In Fig.1, OC/EC ratio reach maximum of approximately 5.6 in midnight on 4 and 13 January 2004. This can be due to the lower EC emission from less activity of mobile vehicles and high organic carbon emission from coal combustion in the night.

### 2.3 Correlations between OC, EC and PM<sub>10</sub>, SO<sub>2</sub>, CO, and O<sub>3</sub>

The daily variations of SO<sub>2</sub>, CO, and O<sub>3</sub> at Beijing during 1–15 January 2004 are also shown in Fig.1. The variation of SO<sub>2</sub> and CO are similar to OC, EC and PM<sub>10</sub> that reach low concentration on 1, 2, 3, 7, 10, 15 January and high concentration on 4, 5, 6, 8, 9, 14 January 2004. This implies that OC, EC, and SO<sub>2</sub>, CO are mainly emitted from proximate sources. Table 4 presents correlation coefficients between OC, EC, and PM<sub>10</sub>, SO<sub>2</sub>, CO and O<sub>3</sub>. The OC, EC have good correlations with PM<sub>10</sub>, which implies that OC and EC are important components of PM<sub>10</sub> in Beijing. In Beijing CO is mainly emitted from motor vehicles (Liu *et al.*, 1999) and SO<sub>2</sub> from coal combustion (Chen *et al.*, 2000). OC, EC, are well correlated to CO and SO<sub>2</sub> which provided another proof that motor vehicles and coal combustion may be dominant sources of OC and EC in PM<sub>10</sub>.

Table 4 Correlation between OC, EC, and PM<sub>10</sub>, SO<sub>2</sub>, CO and O<sub>3</sub>

	SO <sub>2</sub>	O <sub>3</sub>	CO	PM <sub>10</sub>
OC	0.67 <sup>a</sup>	0.18	0.68	0.68
EC	0.72	0.17	0.55	0.65

<sup>a</sup> Correlation coefficient ( $R^2$ ).

But OC and EC are not well correlated with O<sub>3</sub> which means O<sub>3</sub> sources are not mainly from local sources, different with OC, EC. O<sub>3</sub> has noticeable high concentration and OC, EC has low concentration on 1, 2, 3, 7, 10, 15 January when there is strong wind. In troposphere, O<sub>3</sub> concentration usually increases with increase of height (Liu *et al.*, 1999), strong wind can bring down ozone rich air and disperse ground OC and EC. OH and O<sub>3</sub> are required in oxidation reaction to produce SOC (Na *et al.*, 2004). Model calculation by Lu and Khalil (1991) shows that OH concentration reaches maximum in July and minimum in January in the northern hemisphere. This also implies that there is no favorable photochemical reaction condition to produce SOC and the carbonaceous

aerosols in Beijing in winter are dominantly from primary emissions.

## 2.4 Relative contribution to sources of organic carbon and elemental carbon

Coal combustion is one important source of atmospheric particles in typical cities in northern part of China during heating period (Shi *et al.*, 2002). Though coal combustion has not been permitted to use in main urban areas in Beijing since 1999 (Zhang *et al.*, 2002), coal combustion is widely used in the suburb and neighboring areas of Beijing especially in heating period because of its low cost. So coal combustion is an important source for atmospheric aerosol in Beijing (Chen *et al.*, 2000; Dan *et al.*, 2004). Moreover, concern over emissions from mobile sources has been growing along with the amount of vehicles. For example the number of vehicles in Beijing now exceeds 2.1 million. Motor vehicle exhaust is another important source for ambient particles in Beijing in winter (He *et al.*, 2001; Dan *et al.*, 2004). Recent study by using scanning electron microscope (SEM) analysis (Shi *et al.*, 2002) indicate that most PM<sub>10</sub> at Beijing in winter period are from coal combustion and diesel exhaust. So here we try to investigate the contribution of the two major sources using OC/EC ratio with the speculation that carbonaceous aerosols are from primary emission in Beijing in winter period. In Fig.1, the OC/EC ratios reached a lowest value from 1:30 a.m.–16:30 p.m. 12 January 2004 with averaged value of 1.2, when strong wind occurred. OC and EC emission can be due to dominant sources of motor vehicles at this time. So 1.2 is used as the OC/EC ratio from motor vehicles. The OC/EC ratio reach the highest value from 21:00 p.m 4 January to 4:30 a.m. 5 January and 0 a.m. 13 January with averaged 5.6, in the night time, when there is few motor vehicles and dominant source can be due to coal combustion. So 5.6 is used as the OC/EC ratio from coal combustion. Then, a simple source apportionment equation is given as the following:

$$1.2\gamma + 5.6(1 - \gamma) = C_{\text{avg}} \quad (1)$$

where,  $\gamma$  is the fraction of carbonaceous aerosol of motor vehicle origin and  $(1-\gamma)$  is fraction of carbonaceous aerosol of coal combustion origin,  $C_{\text{avg}}$  is averaged OC/EC ratio in day time, night time, or all time. The average OC/EC in all observation period, daytime and night time are 2.3, 2.0, and 2.6, respectively. The calculated contribution from coal combustion and motor vehicle is shown in Fig.3. For the carbonaceous aerosol of Beijing PM<sub>10</sub> in winter period, the motor vehicle source account for 74%, 82% and 68% in total time, daytime and night time, respectively, while coal combustion account for 26%, 18% and 32% in total time, daytime and night time, respectively.

## 3 Conclusions

To understand the diurnal variation characteristics of carbonaceous aerosols in Beijing PM<sub>10</sub>, a real-time observation of OC, EC, and PM<sub>10</sub> is undertaken besides other related parameters such as SO<sub>2</sub>, CO, O<sub>3</sub> during 1–

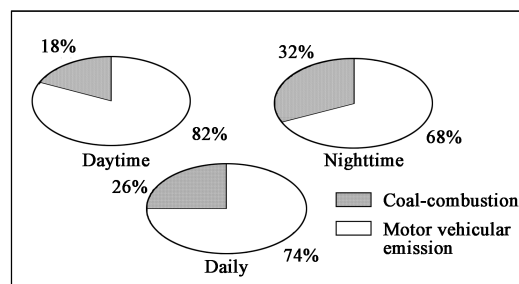


Fig. 3 Sources contribution of carbonaceous aerosol in Beijing PM<sub>10</sub>.

15 January 2004 in urban areas of Beijing. On average, the OC, EC, TC, PM<sub>10</sub> concentrations and OC/EC ratio are  $21.2 \pm 16.0$ ,  $8.9 \pm 5.1$ ,  $30.2 \pm 20.4$ ,  $172.6 \pm 98.3$  and  $2.3 \pm 0.9$   $\mu\text{g}/\text{m}^3$ , respectively. The concentration of OC, EC, PM<sub>10</sub> are low with strong wind and high with not strong wind.

Average OC concentration in nighttime ( $24.9 \pm 19.6$   $\mu\text{g}/\text{m}^3$ ) is 40% higher than that in daytime ( $17.7 \pm 10.9$   $\mu\text{g}/\text{m}^3$ ). Average EC concentrations in daytime ( $8.8 \pm 5.2$   $\mu\text{g}/\text{m}^3$ ) are close to that in night time ( $8.9 \pm 5.1$   $\mu\text{g}/\text{m}^3$ ). The OC/EC ratios in nighttime ranging from 2.4 to 2.7 are higher than that in daytime ranging from 1.9 to 2.0. The OC and EC are well correlated to PM<sub>10</sub>, CO and SO<sub>2</sub>, which implies they have proximate sources. OC and EC are not well correlated with O<sub>3</sub>. The averaged temperature is only 0.7°C in observation period, which is not favorable condition for SOC production. Considering OC/EC ratio in daytime and night time, correlations between OC and O<sub>3</sub>, and meteorological condition, we speculate that OC and EC were emitted as the primary particulate form and no much SOC was produced in winter period in Beijing. Emission of motor vehicle with low OC/EC ratio and coal combustion sources with high OC/EC ratio are dominant sources for carbonaceous in Beijing.

A simple ratio method is used to estimate the relative contribution of sources to carbonaceous aerosols in Beijing PM<sub>10</sub>. Averagely, the motor vehicle and coal combustion account for 74% and 26%, respectively for carbonaceous aerosols in observation period, which suggests the motor vehicle is dominant emission for carbonaceous aerosols in Beijing PM<sub>10</sub> in winter period. The results reveal that motor vehicle sources should be paid attention by China EPA in order to control high level of PM<sub>10</sub> in Beijing effectively.

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## References

- Artaxo P, Castanho A D, Yamasoe M A *et al.*, 1999. Analysis of atmospheric aerosols by PIXE: the importance of real-time and complementary measurements[J]. Nucl Instr Methods Phys Res, B150: 312–321.
- Bhugwant C, Bremaud P, 2001. Simultaneous measurements of black carbon, PM<sub>10</sub>, ozone and NO<sub>x</sub> variability at a locally

- polluted island in the southern tropics[J]. *J Atmos Chem*, 39: 261–280.
- Bond T C, Streets D G, Yarber K F *et al.*, 2004. A technology-based global inventory of black and organic carbon emissions from combustion[J]. *J Geophys Res*, 109: D14203, doi:10.1029/2003JD003697.
- Cabada J C, Pandis S N, Robinson A L, 2002. Sources of atmospheric carbonaceous particulate matter in Pittsburgh, Pennsylvania[J]. *J Air & Waste Manage Assoc*, 52: 732–741.
- Cachier H, Brmond M P, Patrick B M, 1989. Carbonaceous aerosols from different tropical biomass burning sources[J]. *Nature*, 340: 371–373.
- Cao J J, Lee S C, Ho K F *et al.*, 2003. Characteristics of carbonaceous aerosol in Pearl River Delta Region, China during 2001 winter period[J]. *Atmos Environ*, 37: 1451–1460.
- Cao J J, Lee S C, Ho K F *et al.*, 2004. Spatial and seasonal variations of atmospheric organic carbon and elemental carbon in Pearl River Delta Region, China[J]. *Atmos Environ*, 38: 4447–4456.
- Cao J J, Wu F, Chow J C *et al.*, 2005. Characterization and source apportionment of atmospheric organic and elemental carbon during fall and winter of 2003 in Xi'an, China[J]. *Atmos Chem Phys*, 5: 3127–3137.
- Castanho A D A, Artaxo P, 2001. Wintertime and summertime Sao Paulo aerosol source apportionment study[J]. *Atmos Environ*, 35: 4889–4902.
- Chen H, Hu F, Ren L H *et al.*, 2000. Relationship between SO<sub>2</sub> pollution and meteorological conditions in Beijing[J]. *Climatic and Environmental Research*, 5(3): 287–295.
- Chow J C, Watson J G, Chen L-W A *et al.*, 2004. Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols[J]. *Environ Sci Technol*, 38(16): 4414–4422.
- Dan M, Zhuang G S, Lia X X *et al.*, 2004. The characteristics of carbonaceous species and their sources in PM<sub>2.5</sub> in Beijing[J]. *Atmos Environ*, 38: 3443–3452.
- Duan F K, He K B, Ma Y L *et al.*, 2005. Characteristics of carbonaceous aerosols in Beijing, China[J]. *Chemosphere*, 60: 355–364.
- Even A, Khlystov A, Kos G P A *et al.*, 2000. Improvement of BC measurement with the ambient carbon particulate monitor RP5400[J]. *J Aerosol Sci*, 31(S1): 897–898.
- He K B, Yang F M, Ma Y L *et al.*, 2001. The characteristics of PM<sub>2.5</sub> in Beijing, China[J]. *Atmos Environ*, 35: 4959–4970.
- Höller R, Tohno S, Kasahara M *et al.*, 2002. Long-term characterization of carbonaceous aerosol in Uji, Japan[J]. *Atmos Environ*, 36: 1267–1275.
- Jacobson M Z, 2001. Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols[J]. *Nature*, 409: 695–697.
- King A M, 2000. New Directions: TEOMs and the volatility of UK non-urban PM<sub>10</sub>: a regulatory dilemma?[J]. *Atmos Environ*, 34: 3211–3212.
- Kuhlbusch T A J, John A C, Fissan H, 2001. Diurnal variations of aerosol characteristics at a rural measuring site close to the Ruhr-Area, Germany[J]. *Atmos Environ*, 35(1): S13–S21.
- Liu X H, Hong Z X, Li J L *et al.*, 1999. Meteorological and chemical parameters determining the photochemical air pollution in Beijing[J]. *Climatic and Environmental Research*, 4(3): 231–236.
- Liu Y S, Chen R, Shen X X *et al.*, 2004. Wintertime indoor air levels of PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> at public places and their contributions to TSP[J]. *Environment International*, 30: 189–197.
- Long R W, Eatough N L, Mangelson N F *et al.*, 2003. The measurement of PM<sub>2.5</sub> including semi-volatile components, in the EMPACT program: results from the Salt Lake City Study[J]. *Atmos Environ*, 37: 4407–4417.
- Lu Y, Khalil M K A, 1991. Tropospheric OH: Model calculations of spatial, temporal, and secular variation[J]. *Chemosphere*, 23: 397–444.
- Ma C J, Oki Y, Tohno S *et al.*, 2004. Assessment of wintertime atmospheric pollutants in an urban area of Kansai, Japan[J]. *Atmos Environ*, 38: 2939–2949.
- Matsumoto K, Hayano T, Uematsu M, 2003a. Positive artifact in the measurement of particulate carbonaceous substances using an ambient carbon particulate monitor[J]. *Atmos Environ*, 37: 4713–4717.
- Matsumoto K, Uematsu M, Hayano T *et al.*, 2003b. Simultaneous measurements of particulate elemental carbon on the ground observation network over the western North Pacific during the ACE-Asia campaign[J]. *J Geophys Res*, 108(D), 8635, doi:10.1029/2002JD002744.
- Menon S, Hansen J, Nazarenko L *et al.*, 2002. Climate effects of black carbon aerosols in China and India[J]. *Science*, 297: 2250–2253.
- Molnár A, Mészáros E, Hansson H C *et al.*, 1999. The importance of organic and elemental carbon in the fine atmospheric aerosol particles[J]. *Atmos Environ*, 33: 2745–2750.
- Na K, Sawant A A, Song S *et al.*, 2004. Primary and secondary carbonaceous species in the atmosphere of Western Riverside County, California[J]. *Atmos Environ*, 38: 1345–1355.
- Novakov T, Menon S, Kirchstetter T W *et al.*, 2005. Aerosol organic carbon to black carbon ratios: Analysis of published data and implications for climate forcing[J]. *J Geophys Res*, 110: 1–13. doi:10.1029/2005JD005977.
- Pandis S N, 2002. Secondary organic aerosol: precursors, composition, chemical mechanisms, and environmental conditions: Secondary organic aerosol research strategy to apportion biogenic/anthropogenic sources [Z]. An outcome of the first organic aerosol workshop, February 4–5, Desert Research Institute, Reno, Nevada: Fort Lewis College: Durango, CO.
- Salter L F, Parsons B, 1999. Field trials of the TEOM and Partisol for PM<sub>10</sub> monitoring in the St Austell China clay area, Cornwall, UK[J]. *Atmos Environ*, 33: 2111–2114.
- Seinfeld J H, Pandis S, 1998. Atmospheric chemistry and physics: From air pollution to climate change[M]. New York: Wiley. 705–707.
- Shi Z B, Shao L Y, Li H *et al.*, 2002. Physicochemical characterization of the PM<sub>10</sub> in ambient air of Northwestern Beijing urban area during heating period[J]. *Chinese Journal of Environmental Science*, 23(1): 30–34.
- Turpin B J, Huntzicker J J, 1995. Identification of secondary aerosol episodes and quantification of primary and secondary organic aerosol concentrations during SCAQS[J]. *Atmos Environ*, 29: 3527–3544.
- Turpin B J, Saxena P, Andrews E, 2000. Measuring and simulating particulate organics in the atmosphere: problems and prospects[J]. *Atmos Environ*, 34: 2983–3013.
- Wang G C, Bai J H, Kong Q X *et al.*, 2005. Black carbon particles in the urban atmosphere in Beijing[J]. *Adv Atmos Sci*, 22(5): 640–646.
- Watson J G, Chow J C, Houck J E, 2001. PM<sub>2.5</sub> chemical source profiles for vehicle exhaust, vegetative burning, geological material, and coal burning in Northwestern Colorado during

- 1995[J]. *Chemosphere*, 43: 1141–1151.
- Watson J G, 2002. Visibility: science and regulation[J]. *J Air & Waste Manage Assoc*, 52: 628–713.
- Yu J Z, Tung J W T, Wu A W M *et al.*, 2004. Abundance and seasonal characteristics of elemental and organic carbon in Hong Kong PM<sub>10</sub>[J]. *Atmos Environ*, 38: 1511–1521.
- Zhang R J, Wang M X, Fu J Z, 2001. Preliminary research on the size distribution of aerosols in Beijing[J]. *Adv Atmos Sci*, 8(2): 225–230.
- Zhang X Y, Cao J J, Li L M *et al.*, 2002. Characterization of atmospheric aerosol over xian in the south margin of the Loess Plateau, China [J]. *Atmospheric Environment*, 36: 4189–4199.
- Zhang M G, 2004. Modeling of organic carbon aerosol distributions over East Asia in the springtime[J]. *China Particuology*, 2(5): 192–195.
- Zhang M G, Xu Y Y, Zhang R J *et al.*, 2005a. Emission and concentration distributions of black carbon aerosol in East Asia during the spring time[J], *Chinese Journal of Geophysics*, 48(1): 55–61.
- Zhang R J, Arimoto R, An J L *et al.*, 2005b. Ground observations of a strong dust storm in Beijing in March 2002[J]. *J Geophys Res*, 110(D18S06), doi:10.1029/2004JD004589.