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Characteristics of Carbonaceous Particles in Beijing During Winter and Summer 2003

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ABSTRACT

Campaigns were conducted to measure Organic Carbon (OC) and Elemental Carbon (EC) in $PM_{2.5}$ during winter and summer 2003 in Beijing. Modest differences of $PM_{2.5}$ and PM_{10} mean concentrations were observed between the winter and summer campaigns. The mean $PM_{2.5}/PM_{10}$ ratio in both seasons was around 60%, indicating $PM_{2.5}$ contributed significantly to PM_{10}. The mean concentrations of OC and EC in $PM_{2.5}$ were 11.2±7.5 and 6.0±5.0 $\mu g\,m^{-3}$ for the winter campaign, and 9.4±2.1 and 4.3±3.0 $\mu g\,m^{-3}$ for the summer campaign, respectively. Diurnal concentrations of OC and EC in $PM_{2.5}$ were found high at night and low during the daytime in winter, and characterized by an obvious minimum in the summer afternoon. The mean OC/EC ratio was 1.87±0.09 for winter and 2.39±0.49 for summer. The higher OC/EC ratio in summer indicates some formation of Secondary Organic Carbon (SOC). The estimated SOC was 2.8 $\mu g\,m^{-3}$ for winter and 4.2 $\mu g\,m^{-3}$ for summer.

Key words: elemental carbon, organic carbon, $PM_{2.5}$, PM_{10}, secondary organic carbon

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1. Introduction

Carbonaceous aerosols, derived from the combustion process (Cachier, 1998), play an important role in the environment, health and climate (Lighty et al., 2000). Carbon can be present in ambient air as Organic Carbon (OC) and Elemental Carbon (EC), which are the large contributors to $PM_{2.5}$ in the urban atmosphere. OC is a complex mixture of thousands of different organic compounds, containing polycyclic aromatic hydrocarbons and other components. OC can come from direct sources (Primary OC) and gaseous precursors in atmospheric oxidation reactions (Secondary OC) (Pandis et al., 1992). Primary OC originates from biogenic sources and anthropogenic sources. EC has a chemical structure similar to impure graphite and comes mainly from an incomplete combustion process involving carbonaceous material. EC plays an important role in atmospheric chemistry because of its adsorptive and catalytic properties, which can capture other pollutants to react on its surface.

Beijing, the capital and a metropolis of China, has a large population and energy consumption. Though ten-step actions have been taken by local government to reduce atmospheric pollution, including gradual replacement of coal by gas for domestic heating and the prohibition of burning high sulphur and high ash coal, the air pollution is still currently serious with particles (particularly for PM_{10}) as the primary air pollutant. Because carbon is an important atmospheric particle and well related to anthropogenic activities, more research interests have been focused on carbonaceous aerosol research. However, only limited studies about particulate matter have been conducted in China (He et al., 2001; Zhang et al., 2002), let alone continuous measurements of OC and EC in $PM_{2.5}$. In order to study the characteristics of OC and EC in $PM_{2.5}$, campaigns were conducted in Beijing during winter and summer 2003.

2. Experimental methods

2.1 *Measurement site description*

Campaigns were conducted to measure both parti-

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cles and their carbon components from 10 to 28 January (winter campaign) and from 27 August to 12 September (summer campaign) 2003 in Beijing, China. The sampling site was on the roof of the Beijing Municipal Environmental Protection Monitoring Center (BMEMC), about 30 m above the ground. The site is located inside Beijing city, between the west second and third ring roads. Meteorological parameters were also measured during the campaigns, including temperature, humidity, wind speed, and wind direction.

Beijing is located at the northwestern border of the Great North China Plain at 39°48′N latitude and 116°28′E longitude at an altitude of 44 m above mean sea level. Normally in Beijing, north and northwest winds prevail and the temperature is lower than 0°C in winter, and south and southeast winds prevail with a mean temperature of about 20°C in summer.

2.2 *Particle measurements*

Two TEOM (Tapered Element Oscillating Microbalance) particle samplers, R&P1400a manufactured by Rupprecht and Patashnick, Inc., Inc., were used to measure the mass concentrations of PM_{10} and $PM_{2.5}$ at the flow rate of 16.7 L min^{-1} with corresponding sample inlets, respectively. The instruments were operated at 50°C to get rid of water turbulence. It is well documented (Ayers et al., 1999) that this slight heating removes volatile compounds. Hourly-averaged data were collected.

2.3 *Carbonaceous particle measurements*

The concentrations of OC and EC in $PM_{2.5}$ were measured by a thermal technique using the real time Ambient Carbon Particulate Monitor, series 5400 from Rupprecht & Patashnick, Inc. (Rupprecht et al., 1995). The system allowed a direct measurement of carbon through the detection of CO_2 concentration generated by a high temperature oxidation of carbon species volatilized from the collected particulate. A temperature of 340°C was used as the separation point. In this regard, the organic component is defined as that material which volatilizes from the collected particles below or at this temperature. The remaining carbon fraction is elemental carbon along with low vapor pressure, highly polymerized carbon compounds. The most severe drawback of thermal analysis of carbonaceous aerosols is the pyrolitic conversion of organic to soot carbon (charring). The analyzer had two collection cartridges with their inlets and outlets connected to a selector valve that allows one cartridge to be in the collection path while the other is in the analysis loop. The collection and analysis modes are alternated back and forth between the cartridges at a three-hour interval. This allows no interruption in sampling as each collection cartridge in turn is successively sent through a thermal cycle for analysis. The collection path starts with a $PM_{2.5}$ inlet at the flow rate of 16.7 L min^{-1}.

3. Results and discussion

3.1 $PM_{2.5}$ *and* PM_{10} *mass concentrations*

$PM_{2.5}$ and PM_{10} concentrations in Beijing during the winter and summer campaigns in 2003 were measured and modest differences between the two seasons were observed. The mean PM_{10} concentrations in winter and summer were 138.4±95.9 and 133.8±68.6 $\mu g\ m^{-3}$, respectively. The mean $PM_{2.5}$ concentrations in winter and summer were 78.0±68.1 and 80.3±50.7 $\mu g\ m^{-3}$, respectively. The PM_{10} concentration in winter was a little higher than that of summer, while the $PM_{2.5}$ level in winter was similar to that in summer, around 80 $\mu g\ m^{-3}$. The $PM_{2.5-10}$ value (60.4 $\mu g\ m^{-3}$), representing those particles with a diameter between 2.5 μm and 10 μm, in winter was a little higher than that (53.5 $\mu g\ m^{-3}$) in summer. On average, $PM_{2.5}$ constituted 56.3% of PM_{10} concentration in winter, a little lower than the corresponding value of 60.0% in summer. The mean $PM_{2.5}/PM_{10}$ ratio in both seasons was around 60% (between 55% and 60%), indicating that $PM_{2.5}$ contributed significantly to PM_{10}. These ratios were comparable with those measured in four Chinese cities (Wei et al., 1999).

Strong temporal variations of particle mass concentrations were observed in both campaigns, with the maximum level being about 3 times higher than the mean one. Though heavy particle pollution events were often observed in winter, the mean particle mass concentrations are similar for both the campaigns. This suggests that more frequent strong winds in winter enhanced the dispersion of particles and made the mean mass concentrations in winter comparable with that in summer. Generally, the particle levels were affected by both meteorological conditions and source emissions.

3.2 *Concentrations of OC and EC in* $PM_{2.5}$

The summary of OC and EC in the whole campaign (from 10 to 28 January, winter campaign; from 27 August to 12 September, summer campaign) in 2003 in Beijing is given in Table 1. The mean concentrations of OC in PM2.5 were 11.2±7.5 $\mu g\ m^{-3}$ for winter and 9.4±2.1 $\mu g\ m^{-3}$ for summer. The mean concentrations of EC in $PM_{2.5}$ in winter and summer were 6.0±5.0 and 4.3±3.0 $\mu g\ m^{-3}$, respectively. Normally, OC had a higher concentration level than EC. In the present work, the percentage of OC and EC in $PM_2.5$ is calculated according to the following steps: first, we calculated the mean mass concentrations of $PM_{2.5}$, OC and EC during the winter and summer campaigns, respectively; then the mean $PM_{2.5}$ values were divided

Table 1. Comparison of OC and EC in $PM_{2.5}$ in winter and summer 2003.

	OC		EC		
Season	Concentration (μg m^{-3})	Number	Concentration (μg m^{-3})	Number	Mean OC/EC
Winter	11.2±7.5	456	6.0±5.0	456	1.87±0.09
Summer	9.4±2.1	405	4.3±3.0	389	2.39±0.49

Table 2. Comparison of OC and EC in $PM_{2.5}$ between Beijing and other cities.

City	OC (μg m^{-3})	EC (μg m^{-3})	Reference
Seoul	10.3	8.4	Park et al. (2001)
Hong Kong	9.6	4.7	Cao et al. (2003)
Marseille	5.6	2.7	Cachier et al. (2004)
Tokyo	7.8	5.4	Saitoh et al. (2002)
Santiago	52	30.6	Didyck et al. (2000)
Los Angeles	23.4	8.5	Chow et al. (1994)
Athenes	10.7	2.5	Valaoras et al. (1998)
Mexico City	12.8	5.2	Vega et al. (1997)

by the mean values of OC and EC. Thus, the percentages of OC and EC in $PM_{2.5}$ were found to be 14.3% and 7.7% in winter, and 11.7% and 5.4% in summer, respectively. Particle Organic Matter (POM) was also calculated from the conversion of 1.4×OC. Thus all the carbonaceous matter (POM and EC) almost accounted for 30% of $PM_{2.5}$, indicating that the carbon was an important component of the particles. Both the mean concentrations and percentages of OC and EC in $PM_{2.5}$ in summer were lower than those in winter, probably because the sources were stronger or more complicated in winter, such as coal combustion for domestic heating.

The OC and EC concentrations in Beijing were also compared with other cities and the results are shown in Table 2. The OC concentration of Beijing (11.2 μg m^{-3} for winter, 9.4 μg m^{-3} for summer) is higher than Tokyo (7.8 μg m^{-3}), Marseille (5.6 μg m^{-3}), Hong Kong (9.6 μg m^{-3}), Seoul (10.0 μg m^{-3}), lower than Santiago (52.0 μg m^{-3}), Los Angeles (23.4 μg m^{-3}), Athens (23.2 μg m^{-3}), and Mexico city (12.8 μg m^{-3}). Compared with those cities, EC had a similar sequence like OC. Liousse et al. (1996) suggested that fossil fuel combustion was a major source of OC worldwide. Beijing is a typical northern city in China. A large volume of coal is used both industrially and domestically every year in Beijing. For example, the annual energy consumption in 2003 for Beijing equaled 4.7×10^7 t of standard coal. (Beijing Environment Protection, annual report of 2003). Studies of different EC sources showed that motor vehicles contributed much EC to the urban atmosphere (Muhlbaier and Cadle, 1989; Watson, et al., 1990). There are currently more than two million vehicles in Beijing, so vehicle emissions are also very important contributors of carbonaceous aerosol.

Hourly mean concentrations of OC and EC in $PM_{2.5}$ were strongly correlated in winter with a correlation coefficient of 0.97, indicating they had proximate sources in winter, such as coal combustion and vehicle emission. This phenomenon was also found by other studies (Chen et al., 2002). The correlation of OC and EC in summer was relatively lower in summer with a correlation coefficient of 0.90. This suggested some OC from urban non-combustion sources, such as secondary OC in summer. OC and EC were also well correlated with $PM_{2.5}$ in mass concentration, indicating that carbonaceous matter and $PM_{2.5}$ had similar sources.

3.3 *Diurnal variations of OC and EC in* $\mathbf{PM_{2.5}}$

The diurnal variations of OC and EC in $PM_{2.5}$ were generated by calculating the corresponding hourly data of each day according to the time schedule of each campaign (from 0100 to 2400 individually), and these are shown in Fig. 1. The OC and EC levels were affected by the combination of meteorological conditions and source emissions. Because meteorological conditions and emission sources are always changing, the diurnal variations of OC and EC were not fixed. The diurnal variations of OC and EC were used in the present work to describe the specific distributions of the experiment campaigns. Normally there was a larger diurnal variation in winter than in summer. The diurnal concentrations of OC and EC were high at night and low during the day in the winter campaign. This can be explained by the general rule that meteorological conditions play an important role in the diurnal variation via the boundary layer depth (Glen et al., 1996). The meteorological conditions dilute pollutants released at the surface and result in lower concentrations when the boundary layer becomes deeper. The conditions

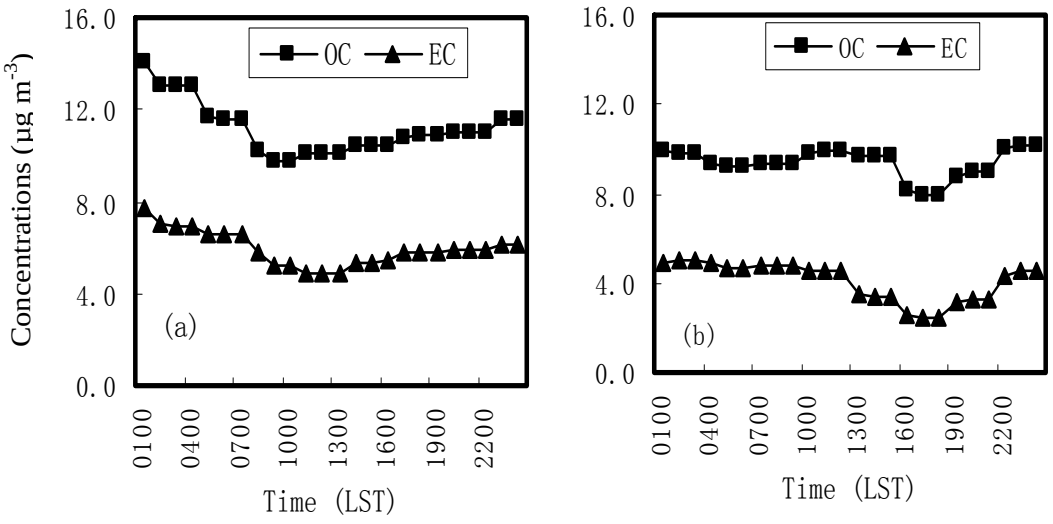

Fig. 1. Diurnal variations of OC and EC in $PM_{2.5}$ in (a) winter and (b) summer in Beijing.

cause the pollutants to accumulate to higher concentrations when the opposite phenomenon occurs. It can be seen form Fig. 1 that the diurnal concentrations of OC and EC are characterized by an obvious minimum in the afternoon in summer. Because the boundary layer usually becomes deeper in the afternoon due to strong solar radiation and turbulent eddies, OC and EC in $PM_{2.5}$ usually exhibited their lowest concentrations during this period. In contrast, OC/EC reached its maximum at this time, indicating the formation of SOC. OC and EC then gradually accumulated to a high level again at night.

Apart from meteorological effects, source emissions (such as coal combustion and vehicle emissions) can also affect the diurnal variations of OC and EC. However, it is hard to explain the source contributions with only one experiment site and limited data. So we do not discuss this here and we will extend our study in the future.

3.4 *Estimation of SOC*

EC comes mainly from incomplete combustion processes involving carbonaceous material and is not formed by reactions involving gaseous hydrocarbon precursors in the air, so EC can be used as a good tracer for primary pollution. OC can be emitted both as primary particles directly from sources and formed as secondary organic carbon (SOC) from chemical reactions. The OC/EC ratio is always used to assess emissions and secondary sources of particles, which is very meaningful in the control of organic pollution. This method takes advantage of the fact that primary OC and EC are mostly emitted by the same sources. Chow et al. (1996) suggested that an OC/EC value of 2.0 could be used to identify the secondary particle formation. The mean OC/EC ratio taken from the literature was 1.87±0.09 in winter campaigns and 2.39±0.49 in summer campaigns, indicating that more SOC is generated in summer. The linear regressions of OC and EC in $PM_{2.5}$ in the winter and summer campaigns are shown in Fig. 2. The intercept represents the non-combustion OC contribution to the primary OC concentration. Compared to winter, the higher intercept value (5.72 μg m^{-3}) in summer may indicate the higher production of SOC in summer. Though we can not tell exactly how much OC/EC comes from the secondary conversion in Beijing, the production of SOC can be calculated from the following equation (Castro et al., 1999):

$$\mathrm{SOC}=\mathrm{TOC}-\mathrm{EC}\times(\mathrm{OC/EC})_{\mathrm{min}}$$

where TOC is the total OC, and $(OC/EC)_{min}$ is the minimum ratio observed and estimated primary ratio. The minimum ratio of OC/EC was 1.4 in winter, while it was 1.2 in summer. The minimum OC/EC ratio was similar to the corresponding slope value in winter (1.45) and summer (0.90). The change in OC versus EC slope may be due to seasonal variations of source strength. Considering the source differences between winter and summer, the two ratios were used as estimates, leading to a mean concentration of 2.8 μg m^{-3} for winter and 4.2 μg m^{-3} for summer, which are close to the corresponding intercepts of Fig. 2a (2.53 μg m^{-3}) and Fig. 2b (5.72 μg m^{-3}), respectively. The estimated SOC consisted of 25.0% OC in winter and 44.7% OC in summer, indicating that the SOC was an important fraction of OC in the Beijing summer.

4. Conclusion

Mass concentrations of OC, EC, $PM_{2.5}$ and PM_{10}

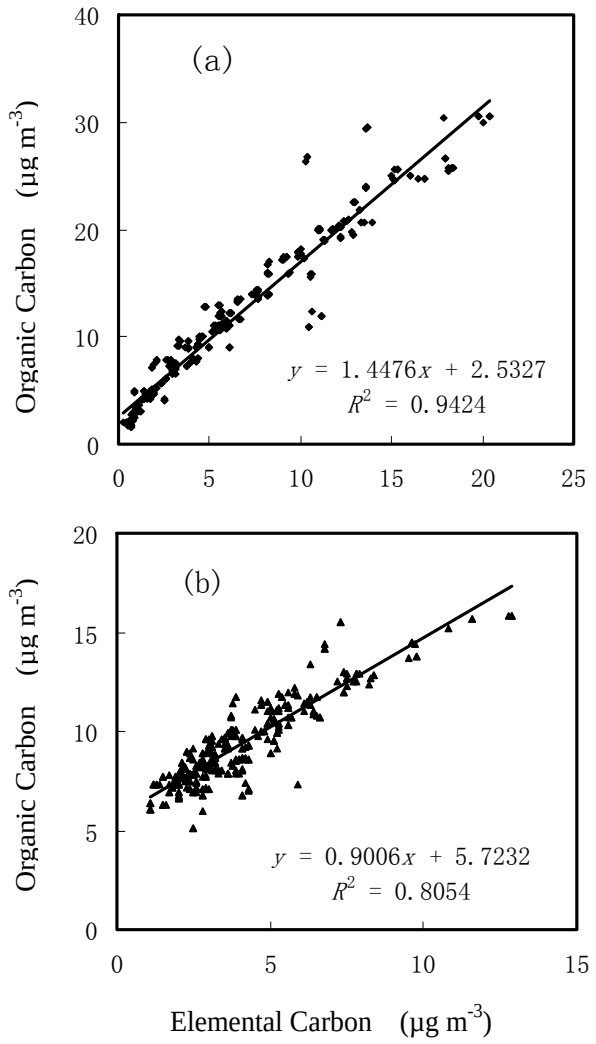

Fig. 2. Correlations of OC and EC in $PM_{2.5}$ in (a) winter and (b) summer.

were measured during winter and summer campaigns in 2003 in Beijing. Modest differences of $PM_{2.5}$ and PM_{10} were observed between the winter and summer campaigns. The mean $PM_{2.5}/PM_{10}$ ratio in both seasons was around 60% (between 55% and 60%), indicating that $PM_{2.5}$ contributed significantly to PM_{10}. Strong temporal variations of particle mass concentrations were observed in both campaigns. Generally, the particle level was affected by both meteorological conditions and source emissions.

OC concentration was found to be higher than EC by about a factor of two. Both concentrations and percentages of OC and EC in $PM_{2.5}$ were lower in summer than in winter, probably because the sources were stronger or more complicated in winter, such as coal combustion for domestic heating. OC and EC were found to be well correlated in winter, indicating that they had proximate sources. The weaker correlation of OC and EC in summer suggested the formation of secondary OC. OC and EC were also well correlated with $PM_{2.5}$ in mass concentration.

Diurnal concentrations of OC and EC in $PM_{2.5}$ in winter were usually found high at night and low during the daytime. The diurnal variations of OC and EC concentrations in summer were characterized by an obvious minimum in the afternoon.

The mean OC/EC ratio was 1.87±0.09 in the winter and 2.39±0.49 in the summer, indicating that there was more SOC generated in the summer. The estimated secondary organic carbon concentration was 2.8 μg m^{-3} for winter and 4.2 μg m^{-3} for summer, which consisted of 25.0% and 44.7% OC in winter and summer, respectively.

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