The characteristics of carbonaceous species and their sources in PM_{2.5} in Beijing

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Received 8 December 2003; accepted 26 February 2004

Abstract

Concentrations of organic carbon (OC) and element carbon (EC) in PM_{2.5} in the urban and rural areas of Beijing were determined and their sources were qualitatively discussed. PM_{2.5} samples were collected at five sites of Beijing during summers and winters of 2001 and 2002 and spring of 2003. Daily average 10.7 ± 3.6 and $5.7 \pm 2.9 \mu\text{g m}^{-3}$ in summer and 36.7 ± 19.4 and $15.2 \pm 11.1 \mu\text{g m}^{-3}$ in winter of 2002 for OC and EC, respectively, were observed in Beijing urban area. The concentrations of carbonaceous species contributed $18.4 \pm 3.5\%$ and $37.2 \pm 12.7\%$ of PM_{2.5} in summer and winter, respectively, of which OC accounted for 70% or more of the total carbon (TC). OC and EC concentrations and their mass percentages in PM_{2.5} were higher in winter than in summer, which could be attributed to the coal consumption of heating period. Organic aerosols would constitute up to 42% of PM_{2.5} in winter based on the evaluation of 1.6 for the ratio of OC to organic particulates. Secondary organic carbon (SOC) were estimated to be more than 50% and up to 95% of total OC in summer based on the minimum OC/EC ratio of 0.9. Comparisons of OC and EC with trace elements, As, Zn, K and Pb, at various sites demonstrated that coal combustion was a dominant source of carbonaceous species of PM_{2.5} in the urban area of Beijing during winter, and biomass burning, traffic and/or industry emission were the major sources of OC and EC in the summer.

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Keywords: Organic carbon; Element carbon; Secondary organic carbon; Prime OC/EC ratio

1. Introduction

Atmospheric fine particles, PM_{2.5}, have been found to play an important role in the human health problem, especially respiratory diseases (Maynard and Maynard, 2002), visibility degradation, and climate change (Penner and Novakov, 1996). Carbonaceous aerosol is a dominant component of fine particle, contributing 20–40% (Rogge et al., 1993), even up to 80% (Nunes and Pio, 1993) to the total mass of fine particles in the urban and industrialized areas and therefore attracts

more and more attention from scientists. It is generally divided into organic carbon (OC) and elemental carbon (EC) (also called black carbon, BC). The terms of OC and EC are operationally defined and do not mean exactly the same literally. For example, “element carbon” may contain a number of organic function groups around the graphite core. Therefore, it must be noted that OC and EC are defined operationally, depending on the method used. For thermal methodology OC and EC were divided based on the different temperatures under which OC or EC is volatilized or oxidized. It has been generally recognized that at or below 400°C in inert gases (Chow et al., 1993) or at 340°C in pure O₂ (Cachier et al., 1989) OC can be totally oxidized with EC intactness, and both OC and EC are volatilized or oxidized above 850°C.

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As a dominant component of the fine particle, carbonaceous aerosol has significant impacts on the global radiation balance and, in turn, on the global climate change through direct and indirect radiation forcing. OC and sulfate aerosols play a key role in the formation of cloud condensation nuclei (CCN) that lead to a higher albedo of cloud and finally the global climate change (Hitzenberger et al., 1999). EC is one of the dominant species that result in the global warming (O'Brien and Mitchel, 2003) and visibility reducing (Lioussé et al., 1996) by absorbing and scattering solar radiation. It has been estimated that the yield of 70% crop in China would be reduced at least by 5–30% due to the reduced solar radiation (Chameides et al., 1999). OC usually contains mutagenic and/or carcinogenic compounds, such as PAHs, PCBs and PCDFs, which are detrimental to human health. EC may also intervene in some important gas-to-particle heterogeneous reactions involving SO_2 , NO_x , O_3 and other gaseous compounds (Novakov, 1984). Thus it is important to study the characteristics and sources of carbonaceous species in $\text{PM}_{2.5}$.

Many studies have been performed in the world focusing on the carbonaceous species of $\text{PM}_{2.5}$ in the ambient atmosphere, and significant progresses have been made either in the methodology or in the observation (concentration, distribution and the effects on global geophysical environment) for OC and EC (Hitzenberger et al., 1999; Offenberg and Baker, 2000; Lim, 2001; Tsapakis et al., 2002; Speer et al., 2003). However, there were only limited studies on the fine particles ($\text{PM}_{2.5}$) (He et al., 2001; Zhang et al., 2002), with fewer on OC and EC in China. To date several studies on carbonaceous particles in PM_{10} or/and $\text{PM}_{2.5}$ in China were reported, which only included Hong Kong (Ho et al., 2002), Taiwan (Lin and Tai, 2001) and Pear River Delta Region (Cao et al., 2003) and almost none in Beijing, the capital of China. There was an early report in 1990 on the particulate air pollution related to OC and EC in Beijing, but not in $\text{PM}_{2.5}$ (Ge et al., 1991). Beijing has become one of the most air-polluted cities in the world in recent years. To understand the reasons and the mechanisms of air-pollution and provide detailed data of the concentration, transformation, and sources of the air-pollutants in Beijing, the spatial and temporal distribution and the possible sources of the carbonaceous species are reported for $\text{PM}_{2.5}$ in Beijing in this study.

2. Experimental

2.1. Sampling

Three urban sampling sites ((1) a traffic site located in the Beijing Normal University (BNU) between the

Second and Third Ring Road of Beijing, (2) an industrial site near the Capital Steel Company (CS), and (3) a residential site, Yihai Garden (YH), located near the South Fourth Ring Road) and two rural suburban sites, Pinggu and Miyun, were designated to represent the varied type of Beijing areas (Fig. 1). Aerosol middle-flow impact sampler (Beijing Geological Instrument-Dickel Co., Ltd., model: (TSP/ PM_{10} / $\text{PM}_{2.5}$)-2, flow rate: 77.591min^{-1}) was employed for $\text{PM}_{2.5}$ sampling. The sampling period was chosen to represent different seasons of summer, winter, and spring, respectively, as below: (1) July–August 2001 and June–July 2002; (2) December 2001–January 2002 and December 2002; and (3) March 2003. The aerosols of $\text{PM}_{2.5}$ were collected daily on the Whatman41 filter membrane (Whatman Company, UK). Among them, for every three days a $\text{PM}_{2.5}$ sample was collected for 12 h on quartz filter ($\Phi 90\text{mm}$, Whatman Company, UK) for OC and EC analysis. The quartz filters were preheated at 500°C for 2 h before sampling to remove the residual carbon. After weighing (Sartorius 2004MP Electronic balance, 0.01 mg) under constant temperature and humidity, the samples were placed in refrigerator at -20°C for late analysis. All the procedures were strictly quality-controlled to avoid any possible contamination of the samples.

2.2. Chemical analysis

OC and TC were measured with C/H/N elemental analyzer (Germany Vario EL, C/H/N model). The procedures were modified from the method described by Chi et al. (1999). OC was measured through the following procedure: 1/8 of each sample filter wrapped with tin foil was fed directly into the combustion tube

Fig. 1. Five sampling sites in Beijing: (a) Miyun; (b) Beijing Normal University (BNU); (c) Yihai Garden (YH); (d) the Capital Steel Plant (CS); and (e) Pinggu.

packed with catalytic material CuO and then was oxidized in He/O₂ mixture (10:1) at 450°C. The oxidized product, CO₂, was detected by the thermal conductivity detector (TCD). This measured carbon value was defined operationally as OC. Another 1/8 of the sample filter was burned in He/O₂ mixture (10:1) at 950°C with correction of inorganic carbonates for the determination of TC. EC was calculated from the difference between TC and OC, i.e. OC = TC – EC.

For the comparison of both OC and EC with other components in PM_{2.5}, we also implemented the element and ion analysis in PM_{2.5}:23 elements, including As, Pb and Zn, those were used in this paper, were analyzed using ICP-AES (Model: ULTIMA, JOBIN-YVON company, French). For the detailed procedures see reference Zhuang et al. (2001). 15 ions, including K⁺, were analyzed with a Dionex 600 IC system that consists of an anion separation column (Dionex Ionpac AS11), a guard column (Dionex Ionpac AG11), a self-regenerating suppressed conductivity detector (Dionex Ionpac ED50) and a gradient pump (Dionex Ionpac GP50). The filters were leached with double-deionized water in an ultrasonic cleaner and the leachate was filtered through 0.45 µm microporous membranes (Ø25 mm), and the filtrate was injected into the IC with polypropylene syringes.

2.3. The reliability of OC and EC determinations

A series of compounds have been employed as standard substances, including caffeine, acetanilide, graphite and calcium carbonate (all of them are analytical grade). Blended mixtures of caffeine, calcium carbonate and graphite (Mixture I) and of caffeine, calcium carbonate and activated carbon (Mixture II) have also been used for testing runs at 450°C and 950°C, respectively. The carbon value determined at 450°C was considered as OC according to the thermogravimetry results of those standard substances including the above two mixtures, which indicated that OC was completely oxidized while graphite maintained intact at 450°C. The analytical results are listed in Table 1. From Table 1, we can see that graphite, taken as a specimen of EC, did not decompose at 450°C. Hence, it is reasonable to select 450°C for the determination of OC. Judging from the standard deviations, the results are satisfactory (Table 1a). The determination accuracy and precision of TC and EC are shown in Table 1a and b, respectively. Comparing the results of this method with those of thermal-optical reflection method (TOR), OC was similar with each other while EC measured by this method was slightly higher than that by TOR (personal communication). The detection limit of carbon was 0.026 mg and the average recovery of OC was 80.4% for seven measurements. The relative standard deviations were 9% and 1.9% for OC and TC, respectively, by

parallel measuring ambient PM_{2.5} sample collected on a quartz filter. To insure the accuracy of the result, the detector response was calibrated with organic standard material (acetanilide) every time before measuring samples.

3. Result and discussion

3.1. Spatial and temporal distribution of OC and EC in Beijing

The average concentrations of PM_{2.5} as well as OC, EC, and TC in Beijing are listed in Table 2. As shown in the table, the carbonaceous species are one of the major components of fine particles in Beijing urban area, averagely accounting for $18.4 \pm 3.5\%$ in summer and $37.2 \pm 12.7\%$ in winter 2002. OC contributed up to $\sim 70\%$ of total carbon (TC). The average concentrations of OC during summer 2002 were 11.5 ± 3.8 , 9.3 ± 3.3 , and $11.2 \pm 3.6 \mu\text{g m}^{-3}$ and of EC were 5.2 ± 2.4 , 6.6 ± 3.2 , and $5.3 \pm 3.1 \mu\text{g m}^{-3}$ at BNU, CS and YH, respectively. During the winter of 2002 OC was 36.6 ± 26.2 , 36.0 ± 21.5 , and $37.5 \pm 11.2 \mu\text{g m}^{-3}$ and EC was 12.9 ± 10.4 , 9.8 ± 6.7 and $21.9 \pm 12.1 \mu\text{g m}^{-3}$ at the three sites, respectively. Generally, the average OC and EC concentrations at the three urban sites of Beijing were almost at the same level in summer and winter, except that EC at YH was higher than that at BNU and CS in winter. This observation indicated that the carbonaceous particle in Beijing urban area might not be influenced strongly by those local factors at various types of sampling sites. However, the higher concentration in winter at the resident area, YH, might be related to the heating period when more coal was used for burning in those denser buildings of the residential areas. Comparing both OC and EC concentrations in urban site, BNU, with the suburban site, Pinggu, OC at Pinggu ($10.3 \pm 1.9 \mu\text{g m}^{-3}$) was lower than that at BNU ($17.1 \pm 4.1 \mu\text{g m}^{-3}$) in summer 2001 and EC seemed to be similar at both sites (4.5 ± 3.3 and $4.9 \pm 5.4 \mu\text{g m}^{-3}$). This was attributed to the higher vehicle emission at the traffic site, BNU. In the spring 2003 there were no significant differences of the concentrations of both OC and EC between the urban site, BNU ($12.56 \pm 5.84 \mu\text{g m}^{-3}$ of OC, $7.8 \pm 7.9 \mu\text{g m}^{-3}$ of EC) and the rural site, Miyun ($15.5 \pm 6.5 \mu\text{g m}^{-3}$ of OC, $7.2 \pm 8.5 \mu\text{g m}^{-3}$ of EC). In winter, however, the concentrations of OC, EC, PM_{2.5}, and other pollutant elements, such as As, Zn, Pb, at Miyun were much higher than that at the urban sites. The observations that the OC and EC concentrations in rural sites were higher in the heating season (winter) and were almost at the same level in non-heating season (summer and spring) indicated that the coal combustion for heating was the dominant source of OC and EC in the rural

Table 1
Reliability of OC and EC determination

(a) OC and TC of standard substances determined at 450°C and 950°C, respectively

<i>T</i> (°C)	Standard substances	Carbon content in parallel runs (%)			Arithmetic average (%)	RSD (%)	Theoretical carbon content (%)	Relative error (%)
		1	2	3				
450	Pure caffeine	49.59	49.39	49.57	49.52	0.22	49.48	+0.07
	Pure calcium carbonate	0.00	0.00	0.00	0.00	0.00	—	—
	Pure graphite	0.00	0.00	0.00	0.00	0.00	—	—
	Mixture I (caffeine, calcium carbonate and graphite)	20.62	20.25	20.53	20.47	0.94	20.57	−0.50
	Mixture II (caffeine, calcium carbonate and activated carbon)	18.24	17.99	18.71	18.31	1.99	^a	^a
950	Pure caffeine	49.48	49.43	49.48	49.46	0.06	49.48	−0.03
	Pure calcium carbonate	11.62	11.78	11.74	11.71	0.71	12.00	−2.39
	Pure graphite	99.35	97.49	99.75	98.86	1.22	100.00	−1.14
	Mixture I	45.23	44.9	45.5	45.2	0.70	45.1	0.22

(b) EC (%) of Mixture I

Carbon	Parallel runs (%)		Arithmetic average (%)	RSD (%)	Theoretical carbon content (%)	Relative error (%)
	1	2				
OC	20.62	20.25	20.44	1.28	20.57	−0.66
OC + EC ^b	40.71	40.36	40.54	0.61	40.52	0.04
EC ^c	20.09	20.11	20.10	0.07	19.81	1.46

^aThe theoretical carbon content was not available because activated carbon is not a pure substance.

^b(OC + EC) was determined with C/H/N elemental analyzer at 950°C after pre-treated by 0.4 mol l^{−1} HCl.

^cEC = (OC + EC) − OC.

areas of Beijing. Possibly, it was the difference in home-heating pattern (lower combustion efficiency of coal due to its individual home-heating pattern in the rural area as compared with the urban area) that leads to the higher OC and EC concentrations in the rural areas compared to the urban sites.

The OC and EC concentrations in both urban and rural sites displayed strong seasonal variation with winter > spring > summer. The highest OC and EC concentrations in winter could be attributed to the higher coal consumption during heating period. It should be noted that OC decreased in 2002 (summer, 11.5 ± 3.8 μg m^{−3}; winter, 36.6 ± 26.2 μg m^{−3}) compared

with that in 2001 (summer, 17.1 ± 4.1 μg m^{−3}; winter, 41.2 ± 20.8 μg m^{−3}). This decrease may be attributed to the new policy of replacing coal with natural gas for heating in the downtown areas since November 2002 and the stricter emission control of vehicles in Beijing.

The comparisons of OC and EC concentrations, mass percentages in PM_{2.5}, and OC/EC ratios in this study with those from other cities over the world are shown in Table 3. It has been seen clearly that OC and EC concentrations as well as their mass percentages in PM_{2.5} in Beijing were the highest among all those locations, indicating that Beijing has been heavily polluted by carbonaceous particles.

Table 2

Average concentrations of PM_{2.5}, OC, EC and secondary organic carbon (SOC) in various seasons in the five sites of Beijing

Period	Site	N ^a	Average concentration ($\mu\text{g m}^{-3}$)				Average mass percentage (%)				OC/EC
			PM _{2.5}	OC	EC	SOC ^b	OC	EC	TC	SOC/OC ^b	
Jul.–Aug. 2001	BNU	8	104.1 $\pm$ 45.1	17.1 $\pm$ 4.1	4.9 $\pm$ 5.4	10.4	19.3 $\pm$ 9.2	4.1 $\pm$ 2.8	23.4 $\pm$ 7.8	59	6.3
	Pinggu	3	121.7 $\pm$ 55.0	10.3 $\pm$ 1.9	4.5 $\pm$ 3.3	6.3	9.7 $\pm$ 5.1	3.7 $\pm$ 2.8	13.4 $\pm$ 4.4	57	4.0
Dec. 2001	BNU	9	257.6 $\pm$ 85.8	41.2 $\pm$ 20.8	31.6 $\pm$ 31.0	17.2	16.6 $\pm$ 7.7	11.3 $\pm$ 10.9	28.0 $\pm$ 15.5	45	7.4
	Miyun	5	683.1 $\pm$ 233.5	72.6 $\pm$ 24.5	37.0 $\pm$ 29.2	39.4	12.6 $\pm$ 7.1	6.1 $\pm$ 4.9	18.7 $\pm$ 10.6	57	3.2
Jun.–Jul. 2002	BNU	10	99.4 $\pm$ 33.9	11.5 $\pm$ 3.8	5.2 $\pm$ 2.4	6.8	12.1 $\pm$ 3.4	5.2 $\pm$ 1.6	17.3 $\pm$ 3.5	57	2.6
	CS	10	86.7 $\pm$ 30.3	9.3 $\pm$ 3.3	6.6 $\pm$ 3.2	3.4	10.9 $\pm$ 1.9	7.6 $\pm$ 2.3	18.4 $\pm$ 3.3	37	1.6
	YH	10	86.8 $\pm$ 29.6	11.2 $\pm$ 3.6	5.3 $\pm$ 3.1	5.8	13.6 $\pm$ 4.0	5.8 $\pm$ 3.1	19.4 $\pm$ 3.7	50	2.5
	BJ urban ^c	30	91.1 $\pm$ 30.9	10.7 $\pm$ 3.6	5.7 $\pm$ 2.9	5.3	12.2 $\pm$ 3.3	6.2 $\pm$ 2.5	18.4 $\pm$ 3.5	48	2.2
Dec. 2002	BNU	9	151.4 $\pm$ 126.8	36.6 $\pm$ 26.2	12.9 $\pm$ 10.4	24.9	29.8 $\pm$ 11.7	10.4 $\pm$ 5.0	40.2 $\pm$ 12.3	64	3.8
	CS	10	171.7 $\pm$ 141.7	36.0 $\pm$ 21.5	9.8 $\pm$ 6.7	27.5	29.0 $\pm$ 13.3	8.8 $\pm$ 6.2	37.7 $\pm$ 18.3	72	4.8
	YH	9	180.0 $\pm$ 77.9	37.5 $\pm$ 11.2	21.9 $\pm$ 12.1	17.7	22.0 $\pm$ 6.1	12.4 $\pm$ 4.3	34.4 $\pm$ 5.6	43	2.2
	BJ urban ^c	28	168.8 $\pm$ 114.1	36.7 $\pm$ 19.4	15.2 $\pm$ 11.1	23.1	26.7 $\pm$ 11.0	10.6 $\pm$ 5.4	37.2 $\pm$ 12.7	59	3.5
Mar. 2003	BNU	3	80.2 $\pm$ 80.2	12.6 $\pm$ 5.8	7.2 $\pm$ 8.5	6.1	24.0 $\pm$ 15.3	7.7 $\pm$ 2.0	31.7 $\pm$ 13.7	58	3.5
	Miyun	5	76.1 $\pm$ 53.4	15.5 $\pm$ 6.5	7.9 $\pm$ 7.9	8.9	23.7 $\pm$ 9.4	9.0 $\pm$ 8.2	32.6 $\pm$ 7.0	59	11.6

^a Number of samples.^b SOC represents secondary organic carbon.^c BJ urban includes three sites of BNU, CS and YH.

Table 3

Literature values of OC and EC for PM_{2.5} in various areas around world

Location	Period	Concentration ($\mu\text{g m}^{-3}$)		Mass percentage (%)		OC/EC	References
		OC	EC	OC	EC		
Beijing, China ^a	6–7/2002	10.7 $\pm$ 3.6	5.7 $\pm$ 2.9	12.2 $\pm$ 3.3	6.2 $\pm$ 2.5	2.2	This study
	12/2002	36.7 $\pm$ 19.4	15.2 $\pm$ 11.1	26.7 $\pm$ 11.0	10.6 $\pm$ 5.4	3.5	This study
Kaohsiung, Taiwan ^a	11/1998–4/1999	10.4	4	15.3	5.9	2.6	Lin and Tai (2001)
Los Angeles, USA ^a	6–9/1987	8.3	2.4				Chow et al. (1994)
	11–12/1987	18.5	7.3				Chow et al. (1994)
Seoul, Korea ^a	6/1994	9.97	7.57				Kim et al. (1999)
Seoul, Korea ^a	11/27–12/09/99	15.2 $\pm$ 9.9	7.3 $\pm$ 5.9			2.4	Park et al. (2002)
Kwangju, Korea ^b	06/07–06/20/00	7.6 $\pm$ 3.7	4.9 $\pm$ 2.1			1.5	Park et al. (2002)
Helsinki, Finland ^a	7/2001–7/2002	3.0	1.2	50 $\pm$ 14% ^d	14 $\pm$ 8%		Viidanoja et al. (2002)
Nairobi, Kenya ^a	3/2000	13 $\pm$ 3	2.3 $\pm$ 0.3			5.7	Gatari and Bomana (2003)
Meru, Kenya ^b	5–6/1999	6 $\pm$ 1	1.4 $\pm$ 0.1			4.3	Gatari and Bomana (2003)
PolyU, HongKong ^a	11/2000–2/2001	9.45 $\pm$ 2.01	5.80 $\pm$ 1.14	18.18	11.16		Ho et al. (2002)
HT, HongKong ^b	11/2000–2/2001	5.52 $\pm$ 1.13	1.36 $\pm$ 0.40	13.04	3.22		Ho et al. (2002)
PRD ^c , China ^a	1–2/2002	14.7 $\pm$ 11.9	6.1 $\pm$ 4.0	19.8 $\pm$ 3.8	8.8 $\pm$ 3.3	2.4	Cao et al. (2003)

^a Urban site.^b Background site.^c PRD is the abbreviation of the Pearl River Delta regions.^d Value is OC $\times$ 1.6.

3.2. Estimate of the secondary organic carbon (SOC)

OC comes from both primary and second origin. Primary sources include those emitted directly from combustion of fossil fuels and biomass (usually as sub-micron particles) and from plant spores and pollen, vegetation debris, tire rubber, and soil organics (usually as coarse particles). Gas-to-particle conversions and/or condensations of volatile organic compounds are known

as secondary sources of OC. EC is essentially emitted directly from combustion of fossil fuels and biomass. As EC is resistant to the chemical reactions, it is a good indicator of primary anthropogenic pollutants and it has been used to estimate the second OC (Huntzicker et al., 1986; Turpin and Huntzicker, 1991; Strader et al., 1999; Lin and Tai, 2001; Viidanoja et al., 2002). The principle for the estimate is that there is a prime OC/EC ratio ((OC/EC)_{pri}) to be the representative of a given area based on

the fact that EC and primary OC, especially in fine particles, often have the same origins. When the measured OC/EC ratio in the ambient aerosols is higher than the primary (OC/EC)_{pri}, the additional OC is considered to be the secondary one. Turpin and Huntzicker (1995) suggested an equation below to identify the SOC based on the hypothesis mentioned above

$$\text{OC}_{\text{sec}} = \text{OC}_{\text{tol}} - \text{EC} \times (\text{OC/EC})_{\text{pri}}, \quad (1)$$

where OC_{sec} is the SOC, and OC_{tol} the measured ambient total OC. The prime organic carbon (OC_{pri}) could hence be calculated from the formula EC × (OC/EC)_{pri}. However, there still are difficulties in estimating the ratio (OC/EC)_{pri} accurately for a given area. First, the ratio (OC/EC)_{pri} varies with various sources and the assumed prime ratio, (OC/EC)_{pri}, would have a uncertainty. Secondly, the prime ratio is influenced by meteorological conditions, and it would have the diurnal and seasonal fluctuations (Turpin and Huntzicker, 1995). Thirdly, it is actually impossible to distinguish the OC_{pri} from the second one. Anyway, Turpin and Huntzicker (1991) measured the ambient OC/EC ratios and then obtained a mean prime OC/EC ratio of 2.2 ± 0.2

Fig. 2. The relationship of OC and EC at various sites in different seasons. The line represents (OC/EC)_{min} = 0.9.

Table 4
Literature values of secondary organic carbon (SOC)

Site	Season	SOC ($\mu\text{g m}^{-3}$)	SOC/OC (%)	References
Birmingham ^a	Winter	0.63	17	Castro et al. (1999)
Birmingham ^a	Summer	3.1	65	Castro et al. (1999)
Coimbra ^a	Winter	3.61	37	Castro et al. (1999)
Coimbra ^a	Summer	2.58	50	Castro et al. (1999)
Los Angeles ^b	Summer		40–80	Turpin and Huntzicker (1995)
Kaohsiung ^b	Winter	4.2	40	Lin and Tai (2001)

^aThe particulate samples were PM₁₀.

^bThe particulate sample were PM_{2.5}.

under the specific conditions (lack of sun, intermittent drizzle, low ozone concentration and an unstable air mass) in that the photochemical activity and, in turn, SOC formation was minimal. Lim (2001) obtained the prime OC/EC ratio of 2.1 with the same approach. Castro et al. (1999) suggested that (OC/EC)_{pri} could be replaced by (OC/EC)_{min} if the (OC/EC)_{min} contain exclusively the primary carbonaceous compounds, and the former equation could be written as below

$$\text{OC}_{\text{sec}} = \text{OC}_{\text{tol}} - \text{EC} \times (\text{OC/EC})_{\text{min}}. \quad (2)$$

This equation would be reasonable if the minimum ratios, (OC/EC)_{min}, are stable and reproducible at various locations in different seasons.

Fig. 2 represents the relationship of OC with EC at five sampling sites of Beijing in the summer and winter of 2001 and 2002. Similar minimum OC/EC ratios were observed for various sites in different seasons (0.8 in both winter and summer at BNU, 1.1 in spring at BNU, 0.9 at CS, 0.9 in winter and 1.0 in summer at Yihai, 1.2 at Miyun in winter and 1.0 in summer at Pinggu). Which ratio (0.8 or 0.9) is more reasonable to be chosen as the prime OC/EC ratio? Strader et al. (1999) reported that the formation probability of the secondary organic aerosol is very high if OC/EC ratio exceeds 2.9. They chose those samples with OC/EC ratio < 2.9 to perform a least-squares regression and have a primary OC/EC ratio. Following Strader's procedure we took 58 samples in which the measured OC/EC ratios were < 2.9, of the total 91 PM_{2.5} quartz samples in this study, for the statistical analysis, and found a linear equation of $\text{OC} = 0.9027\text{EC} + 7.6877$ with the correlation coefficient (R^2) of 0.7505. Therefore, we selected the slope of 0.9 for the plot of OC vs. EC as the prime OC/EC ratio in estimating the prime OC and SOC. It must be noted that the minimum OC/EC ratios at the three urban sites, BNU, CS, and YH, occurred on the same day, i.e. on 29 June in the summer 2002 and on 15 December in the winter 2002. We found that on these two days the O₃ concentrations, the visibility, and the wind speed were very low and the secondary formation of OC must be negligible. Thus, it would be reasonable to use the minimum ratio on these two days as the prime ratio. The

calculated average concentrations of SOC at various sampling sites using this minimum OC/EC ratio are given in Table 2.

As the data indicated, SOC in Beijing contributed to the total OC in a great measure, mostly more than 50% with the maximum of 95%. Table 4 also listed some data of SOC in other locations. It would be

interesting to know that SOC was higher in winter than in summer in Beijing, which is contrary to those European cities, Birmingham and Coimbra, where SOC was higher in summer than in winter. This might be due to the great coal consumption for heating in winter at Beijing, which would increase the emission of semi-volatile organic compound and organic gas.

Fig. 3. Correlations between OC, EC, As, Zn, K and Pb at three urban sites (CS, Yihai and BNU) in Beijing.

The results demonstrated that the coal combustion could likely be the dominant sources of the organic aerosols in Beijing.

3.3. The sources of OC and EC in Beijing

We compared OC and EC with those pollution elements and ion data generated from ICP-ACE and IC analysis in the same PM_{2.5} samples to discuss qualitatively the sources of OC and EC in Beijing. The relationship of elements, As, Zn, K, and Pb, with OC and EC at three urban sampling sites (CS, YH, and BNU) is shown in Fig. 3. As mentioned above, EC is essentially emitted directly from combustion of fossil fuels or/and biomass and it is usually regarded as a marker of local traffic (Song et al., 2001). K⁺ is known as a tracer of biomass combustion; Zn and Pb were usually identified to relate with motor vehicle, waste incinerating and industrial sources, as reported the literature (Lee et al., 1999; Yang et al., 2000; Gao et al., 2002) with different statistical analysis, such as factor analysis (FA), enrichment factor analysis (EF) and positive matrix factor analysis (PMF). From Fig. 3 it could be seen clearly that OC correlated closely with EC ($R = 0.63$), As ($R = 0.82$), Zn ($R = 0.74$), Pb ($R = 0.78$) and K ($R = 0.72$) in winter at the traffic site, BNU, while there were very poor correlations ($R < 0.3$) between them in summer. It also illustrated that EC correlated positively with K ($R = 0.67$) and Zn ($R = 0.80$) and poorly with As ($R = 0.18$) during summer. This would suggest that in winter, at the downtown areas with heavy traffic OC and EC, came mostly from coal combustion, vehicle exhaust, and biomass burning all together, while in summer it was vehicle exhaust and biomass rather than coal combustion that were the major sources of EC. However, at the industrial site, the capital steel plant (CS), there was no such seasonal difference in the relationship between the above species. Very strong correlations of OC and EC with other elements were found ($R = 0.7–0.97$) in both winter and summer at this site. This could be explained by the fact that the coal combustion is a routine action in the Capital Steel Plant over the entire year and the coal combustion and industry emission could be the major sources of OC and EC in this area in summer and winter. It should be noted that it might be more reasonable to consider Zn and Pb was the marker of the industry emission in this area rather than the vehicle exhaust, because the traffic was not busy. At the residential site, YH, the OC was not related well with EC in both summer and winter. However, there was a good correlation of OC with As (0.60), Zn (0.79) and Pb (0.79) in winter in this area, indicating that the three sources, coal combustion, vehicle exhaust and biomass, burning were to be the major sources of OC in this area during winter. Industry emission is a possible source of OC in this residential

area in winter because YH is located downwind of CS, the Capital Steel plant, and it is inevitable to be affected by CS. This can be demonstrated by the good relationship between OC and As ($R = 0.74$) in this area even in summer when heating does not take place.

4. Conclusion

The carbonaceous species, including OC and EC, were the major components in PM_{2.5} in Beijing. The OC dominated the carbonaceous compounds, accounting for 70% or more of the TC. There was a significant seasonal variation of OC and EC with higher concentrations and higher mass percentage in PM_{2.5} in winter at all sites in Beijing. This could be attributed to the coal burning for heating in winter. SOC was estimated to be more than 50% and even up to 95% of OC in summer based on the minimum OC/EC ratio of 0.9. There is no significant difference of average OC and EC concentration at the urban areas in Beijing. Comparisons of OC and EC with trace elements, As, Zn, K, and Pb at various sites demonstrated that coal combustion was a dominant source of carbonaceous species of PM_{2.5} in the urban areas of Beijing during winter while traffic, biomass burning, and/or industry emission were the major sources of OC and EC in the summer.

Acknowledgements

The author would like to thank Yele Sun and Ying Wang of the Center for Atmospheric Environmental Study of Beijing Normal University, Beijing, China, for their help in experiment and sharing their data. This work was supported by National Science Foundation of China (Grant Nos. 29837190, 20077004, 3023030), Beijing Natural Science Foundation (Grant No. 8991002, 8041003) and partly funded by LAPC, The Institute of Atmospheric Physics, Chinese Academy of Science, and the Swedish Agency for Research Cooperation with Developing Countries (SAREC) of the Swedish International Development Cooperation Agency (SIDA) through the Asian Regional Research Program on Environmental Technology (ARRPET) at the Asian Institute of Technology.

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