Available online at www.sciencedirect.com
SCIENCE DIRECT®

ELSEVIER

Atmospheric Environment 39 (2005) 3967–3976

ATMOSPHERIC
ENVIRONMENT

www.elsevier.com/locate/atmosenv

Seasonal trends in PM2.5 source contributions in Beijing, China

Mei Zheng[a,*], Lynn G. Salmon[b], James J. Schauer[c], Limin Zeng[d],
C.S. Kiang[d], Yuanhang Zhang[d], Glen R. Cass[a,✠]

[a]*School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332-0340, USA*
[b]*Environmental Science & Engineering Department, California Institute of Technology, Pasadena, CA 91125, USA*
[c]*Environmental Chemistry and Technology Program, University of Wisconsin-Madison, Madison, WI 53706, USA*
[d]*College of Environmental Sciences, Peking University, Beijing 100871, China*

Received 25 August 2004; accepted 7 March 2005

Abstract

The 24-h PM2.5 samples (particles with an aerodynamic diameter of 2.5 μm or less) were taken at 6-day intervals at five urban and rural sites simultaneously in Beijing, China for 1 month in each quarter of calendar year 2000. Samples at each site were combined into a monthly composite for the organic tracer analysis by GC/MS (gas chromatography/mass spectrometry). Compared to the data obtained from other metropolitan cities in the US, the PM2.5 mass and fine organic carbon (OC) concentrations in Beijing were much higher with an annual average of 101 and 20.9 $\mu g\,m^{-3}$, respectively. Over one hundred organic compounds including unique tracers for important sources were quantified in PM2.5 in Beijing. Source apportionment of fine OC was conducted using chemical mass balance receptor model (CMB) in combination with particle-phase organic compounds as fitting tracers. Carbonaceous aerosols and major ions (sulfate, nitrate and ammonium) constituted 69% of PM2.5 mass on average. The major sources of PM2.5 mass in Beijing averaged over five sites on an annual basis were determined as dust (20%), secondary sulfate (17%), secondary nitrate (10%), coal combustion (7%), diesel and gasoline exhaust (7%), secondary ammonium (6%), biomass aerosol (6%), cigarette smoke (1%), and vegetative detritus (1%). The lowest PM2.5 mass concentration was found in January (60.9 $\mu g\,m^{-3}$), but the contribution of carbonaceous aerosol to PM2.5 mass was maximal during this season, accounting for 57% of the mass. During cold heating season, the contributions from coal combustion and biomass aerosol to PM2.5 mass increased, accounting for 20.9% of fine particle mass in October and 24.5% in January. The contribution of the biomass aerosols peaked in the fall. In April 2000, the impact of dust storms was so significant that dust alone constituted 36% of PM2.5 mass. On average, the model resolved 88% of the sources of the PM2.5 mass concentrations in Beijing.

Keywords: Source apportionment; Fine particles; Organic tracers; CMB; China

---

1. Introduction

Beijing, the capital of China, is facing very serious air pollution problems including extremely high concentrations of suspended particles in the atmosphere. A set of

---

*Corresponding author. Tel.: +1 (404) 8941633;
fax: +1 (404) 8945638.
E-mail address: mzheng@eas.gatech.edu (M. Zheng).

✠Deseased.

1352-2310/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.atmosenv.2005.03.036

national air quality standards for PM10 (particles with an aerodynamic diameter of 10 μm or less) has been promulgated in China in 1996; however, unlike the US, China has not regulated PM2.5 yet (Wei et al., 1999). The annual average concentration of PM2.5 measured at five sites in Beijing in the present study is 101 $\mu g\,m^{-3}$, similar to the average value reported by He et al. (2001) of 115 $\mu g\,m^{-3}$ at Chegongzhuang site and 127 $\mu g\,m^{-3}$ at Tsinghua site. By comparison, the measured average concentration of PM2.5 is only about 21 $\mu g\,m^{-3}$ in Houston (Frazier et al., 2002), 15.5 $\mu g\,m^{-3}$ in Pittsburgh (Wittig et al., 2004), and 21.0 $\mu g\,m^{-3}$ in Baltimore (Landis et al., 2001) in the US, and ranges from 3.7 to 44.9 $\mu g\,m^{-3}$ in 21 European study centers (Hazenkamp-von Arx et al., 2004). An obvious impact of such high concentrations of airborne fine particles is severe visibility reduction. Davis and Guo (2000) studied the characteristics of airborne particulate matter in five cities in China and indicated that the low visibility in these cities was primarily due to fine carbon-containing particles. It was reported that the mean of hourly averages of the light scattering coefficient and light absorption coefficient in Beijing during a field study in June 1999 was significantly higher than values measured in urban regions of the US and the fine combustion-related particles are responsible for most of the local light scattering in Beijing (Bergin et al., 2001). As there is great need to control particulate matter concentrations in Beijing to improve visibility, protect human health, and reduce ecological damage (Chameides et al., 1999), a clear understanding of the composition, concentration, and sources of these airborne fine particles is required. Source apportionment, which links sources to the measured air quality, is critical in the development of effective and efficient air pollution control measures.

In this paper, samples collected in January, April, July, and October 2000 simultaneously at five sites in Beijing including rural and urban areas were analyzed by GC/MS to obtain the detailed information of particle-phase and solvent-extractable organic compounds in Beijing PM2.5, which were used as tracers for source apportionment of PM2.5. A recent study by Dan et al. (2004) aimed to identify the sources of PM2.5 in Beijing using elemental carbon (EC), organic carbon (OC), and trace elements. However, this is the first time that the organic tracer based CMB model is applied to quantitatively apportion the sources that contribute to fine organic carbon and fine particle mass concentrations in Beijing.

2. Experimental methods

2.1. Sampling

PM2.5 samples were collected from five sites in Beijing with samplers fabricated from commercial sampler components that have been extensively used in the past (Salmon et al., 1994; Chowdhury et al., 2001). The sampling locations in this study are shown in the Supplemental Materials as Fig. S1. Samples collected at DongSi EPB (XY), a site of Beijing Environmental Protection Bureau (EPB), were obtained on a roof of a one-story building in central Beijing in an area of heavy traffic, shops, and restaurants located nearby. The Peking University site (BJ), 13 miles NW of central Beijing, is located on the roof of a five-story building in the campus of Peking University, which is surrounded by heavy traffic, residential apartments, research institutes, and electronic companies. The site close to the airport (NB) is 19 miles NE of central Beijing. The sampler is on the roof of a one-story office building, which is surrounded by light industrial activities with little traffic. The samples in Yong Le Dian site (CH), 25 miles SE of central Beijing, which is surrounded by light industrial and residential activities, were collected on top of a 2nd story building close to a busy street. The Ming Tombs site (OT) is a background site, located 34 miles NW of central Beijing. The sampler was placed on the roof of a one-story building near the entrance to the Ming Tombs, where heavy traffic only occurred during the weekends with high tourist activity.

The 24-h PM2.5 samples were collected simultaneously at the above five sites at 6-day intervals in January, April, July, and October 2000. The details of the sampling procedures are described elsewhere (Salmon et al., 1994). In brief, air was pulled through a cyclone separator at a flow rate of 23 lpm to remove particles with aerodynamic diameter larger than 2.5 μm. Fine particles were then collected simultaneously on three parallel filters (two Teflon filters and one quartz fiber filter, 47 mm in diameter) during each 24-h sampling period. One Teflon filter is used for the measurement of fine mass, ionic analysis including sulfate, nitrate, and chloride by IC (ion chromatography), and ammonium ion by colorimetric method. The measurement of metals by X-ray fluorescence (XRF) is from the other Teflon filter. The quartz fiber filter is used for the analyses of organic carbon, EC, and detailed organic speciation. One punch (1.5 cm^2) was taken from each quartz fiber filter for the analysis of EC and OC by the NIOSH thermal-optical method (Birch and Cary, 1996). The remaining quartz fiber filters at each site of each month were combined to form a monthly composite for the organic speciation analysis by GC/MS.

2.2. Organic speciation analysis

The experimental procedure is similar to those used in the previous studies and summarized briefly here (Schauer et al., 1996; Zheng et al., 2002). The mixture of isotopically labeled compounds was spiked into each sample prior to extraction, including benzaldehyde-d_6, dodecane-d_{26}, decanoic acid-d_{19}, phthalic acid 3,4,5,6-d_4, acenaphthene-d_{10}, levoglucosan-$^{13}C_6$ (carbon-13 uniform labeled compound), hexadecane-d_{34}, eicosane-d_{42}, heptadecanoic acid-d_{33}, 4,4′-dimethoxybenzophenone-d_8, chrysene-d_{12}, octacosane-d_{58}, ααα-20*R*-cholestane-d_4, cholesterol-2,2,3,4,4,6-d_6, dibenz(*ah*)anthracene-d_{14}, and hexatriacontane-d_{74}. Samples were ultrasonically extracted twice with hexane (Fisher Optima Grade), then three times with bezene/isopropanol (2:1 mixture) (isopropanol: Fisher Optima Grade; benzene: E & M Scientific Ominisolv benzene). Benzene was redistilled prior to use. After filtration through a column packed with prebaked glass wool, the extracts were concentrated to about 5 mL by a rotary evaporator. The volume of the extracts was further blown down to about 0.5 mL under high purity nitrogen. Each extract was split into two fractions, with one fraction derivatized by diazomethane to convert organic acids to their methyl ester analogues before GC/MS analysis and the other fraction was stored in the freezer for future use.

2.3. GC/MS analysis

One microliter of each derivatized sample was injected into the GC/MS on a Hewlett-Packard GC/MSD (6890 GC and 5973N MSD) for identification and quantification of organic compounds. The column used was a HP 5 MS capillary column (coated with 5% phenyl methyl siloxane). The GC conditions were: isothermal hold at 65 °C for 10 min, temperature ramp of 10 °C min^{-1}–300 °C, isothermal hold at 300 °C for 22 min, and He as carrier gas with a flow rate of 1.0 mL min^{-1}. The GC/MS interface temperature was 300 °C. Organic compounds passing the interface were ionized by electron impact (70 eV) and scanned from 50 to 500 amu. Hundreds of authentic quantification standards have been prepared for the identification and quantification of organic compounds detected in the ambient fine particulate samples.

One hundred and 19 organic compounds were measured including alkanes, organic acids, polycyclic aromatic hydrocarbons (PAHs), and tracer compounds such as retene and levoglucosan. The uncertainties (one standard deviation) for the quantification of organic compounds in source and ambient fine particles were determined to average ±20%. For PM2.5 mass, OC, EC, Al, and Si, the average uncertainties were 3.1%, 7.0%, 14.8%, 4.7%, and 1.3%, respectively.

2.4. Receptor model approach

A receptor-oriented chemical mass balance model was used in this study to apportion the sources contributing to fine OC in Beijing. A mass balance is constructed assuming that the concentrations of chemical mass balance species in the atmosphere are linear sums of each contributing source using the US EPA CMB7.0 software (Environmental Protection Agency (EPA), 1987). The selection of species used in the model was based on the previous work by Schauer et al. (1996) and Schauer and Cass (2000).

The technique of source identification using organic components characterized by GC/MS has been well demonstrated (Cass, 1998). The organic molecular marker technique for diagnosing the contribution of the air pollution sources is especially important for those regions like Beijing with high emissions of carbonaceous materials. Since fully developed local source profiles for Beijing are not available, the present study employs the best estimates of local source profiles that are available with the ambient measurements. Since dust in spring and coal emissions in cold season have significant influence in this region, efforts were made to obtain the true local source profiles for the CMB analysis. The dust profile was constructed by the EC, OC, Al, and Si data extracted from the April 25, 2000 sample when a severe dust event occurred. For April ambient samples, this reconstructed profile was employed, while during other seasons, the dust profile was replaced by the one reported by Zheng et al. (2002). The coal profile was obtained from the analysis of direct emissions from the burning of Datong coal in a small cooking oven in a house in Yungang, China, which were collected by placing the inlet of the sampler into the diluted smoke plume. The chemical characteristics of three stages of the coal emissions including initial, middle, and final stages are shown in the Supplemental Materials as Table S1 along with the organic speciation results from the initial stage in Table S2. Due to the fact that wood chips were used to light the coal fire, the measured coal smoke profile contained some wood smoke. In order to correct the profile to remove the wood smoke contribution, the coal profile was modified by removing the wood smoke using the measured levoglucosan as a tracer for the wood smoke. The modified coal smoke profile is presented in the Supplemental Materials as Table S3. This modified profile was used in CMB for estimating the coal burning contribution. The source profiles describing diesel engine exhaust, noncatalyst-equipped gasoline-powered vehicle exhaust, vegetative detritus, biomass aerosol, and cigarette smoke were taken from previous studies in North America (Hildemann et al., 1991; Rogge et al., 1993; Schauer et al., 1999, 2001, 2002). Noncatlyst-equipped gasoline-powered vehicle profile is used because those vehicles emit much more particulate matter than catalyst-equipped cars. Tracers including *iso*-nonacosane, *anteiso*-triacontane, and *iso*-hentriacontane are used for the cigarette smoke source in the present study. Thus, vegetative detritus or resuspended soil can be contributing to what appears to be cigarette smoke. For those sources with the source profiles representing the emission characteristics in the US, the source contribution results in the present study should be taken as the best estimate that one could have at this time.

3. Results and discussion

More than 100 organic compounds including *n*-alkanes, PAHs, *n*-alkanoic acids, *n*-alkenoic acids, resin acids, aliphatic and aromatic dicarboxylic acids, and key tracer organic compounds such as levoglucosan were identified and quantified in each sample. The organic compounds that have been tested to conserve during the transport (Schauer et al., 1996) as well as Al, Si, OC and EC data previously quantified were applied in the CMB model to apportion the source contributions to fine OC. Though OC measurement is known to be associated with sorption and desorption artifacts, the organic tracer measurements are not affected because the selected fitting species in the model are primarily in the particulate phase (Schauer et al., 1996; Turpin et al., 2000). Same filter was used for collecting ammonium nitrate and PM2.5 mass, so the ammonium nitrate artifacts do not affect the mass closure. The goodness-of-fit indicators of the model results provided by the CMB7.0 software include R^2 (target >0.8), χ^2 (target <4), degree of freedom (DF, target >5), percent of aerosol mass explained by the sources (target between 80% and 120%), C/M ratio (ratio of calculated to measured concentration, target 0.5–2.0), and absolute value of R/U ratio (ratio of residual to uncertainty, target <2). The CMB results of this study are statistically significant as shown by the average R^2, χ^2, DF, and the percent mass explained as 0.97 ± 0.02, 2.95 ± 0.72, 25 ± 3, and $61 \pm 20\%$ ($n = 20$), respectively. There are about 30 fitting species in the CMB model. In each sample, a C/M ratio and an R/U ratio for each fitting species are available from the CMB output. The average C/M ratio is 0.96 ± 0.39 ($n = 666$) while the average absolute R/U ratio is 1.26 ± 0.91 ($n = 666$). The monthly averages of EC, OC, ions, and organic compound concentrations measured at five sites in Beijing are shown in the Supplemental Materials as Table S4. Due to concerns over the ability of the model to accurately separate the contribution of diesel and gasoline vehicle particulate matter emissions in Beijing using US source profiles, the sum of diesel and gasoline exhaust is reported in the present study.

3.1. Fine particle organic carbon apportionment

OC concentrations in PM2.5 in Beijing during January, April, July, and October 2000 at five sites ranged from $13\,\mu g\,m^{-3}$ at the OT site in summer to $31\,\mu g\,m^{-3}$ at the NB site in winter, with an annual average of $20.9\,\mu g\,m^{-3}$. A much higher OC/EC ratio (7.0 on average) can be found in Beijing PM2.5 compared to a ratio of 1.8 in Houston, TX (Frazier et al., 2002).

Carbonaceous material is the largest component in Beijing fine particles, constituting 17–65% of PM2.5 mass (with an average of 35%), while the sum of sulfate, nitrate, and ammonium concentrations accounted for 24–47% of PM2.5 mass concentration, averaging 34% (Fig. 1). Thus, carbonaceous material plus ions constituted 44–89% of PM2.5. However, a distinct seasonal pattern could be seen with the highest percentage of carbonaceous aerosol in PM2.5 in January (57%) and the lowest level in April (21%), while the highest percentage of the sum of sulfate, nitrate, and ammonium in PM2.5 was found in July (42%), mainly due to secondary aerosol formation.

The measured OC concentrations were high in January and October and low in July, however, the PM2.5 mass concentrations showed a very different pattern. The average PM2.5 mass concentration in January, April, July, and October 2000 was 60.9, 140, 99.0, and $106\,\mu g\,m^{-3}$, respectively. The source apportionment results of fine particulate OC are shown in Table 1.

The major sources contributing to OC in Beijing PM2.5 on an annual basis were identified by the CMB as diesel and gasoline exhaust ($17.3 \pm 6.9\%$), biomass aerosol ($16.1 \pm 18.1\%$), dust ($11.7 \pm 8.1\%$), coal combustion ($9.8 \pm 3.9\%$), cigarette smoke ($3.1 \pm 2.2\%$), and vegetative detritus ($1.4 \pm 0.9\%$). However, sources exhibited distinct seasonal variations (Fig. 2a). The importance of biomass aerosol and coal combustion became obvious in October and January, accounting for 30% of OC in January and 50% in October. It is not surprising to see the dramatic increase of biomass aerosol contribution in October (37% of OC) because it is also the harvesting season when crop residues/straw are actively burned. This corresponds well to the findings by He et al. (2001), who reported that biomass burning activity is widely present around Beijing and expected to peak during mid-October–mid-November. However, similar to the southeastern US, no significant wood burning contribution to fine OC concentrations was found in July (Zheng et al., 2002). Coal was used quite heavily in Beijing, not only for power generation, industry, and central heating system, but also for heating in many old houses. The CMB results revealed that coal combustion explained 12.7% of measured OC in October and 13.9% in January. The coal profile was generated from burning Datong coal in a small cooking oven and the emission was sampled by sticking the inlet of the sampler directly into the smoke. Thus, the sampled coal smoke was actually the coal smoke with high carbon coal fly ash and does not represent coal smoke from coal burning with high efficiency burners that removes all carbon and emits particulate matter

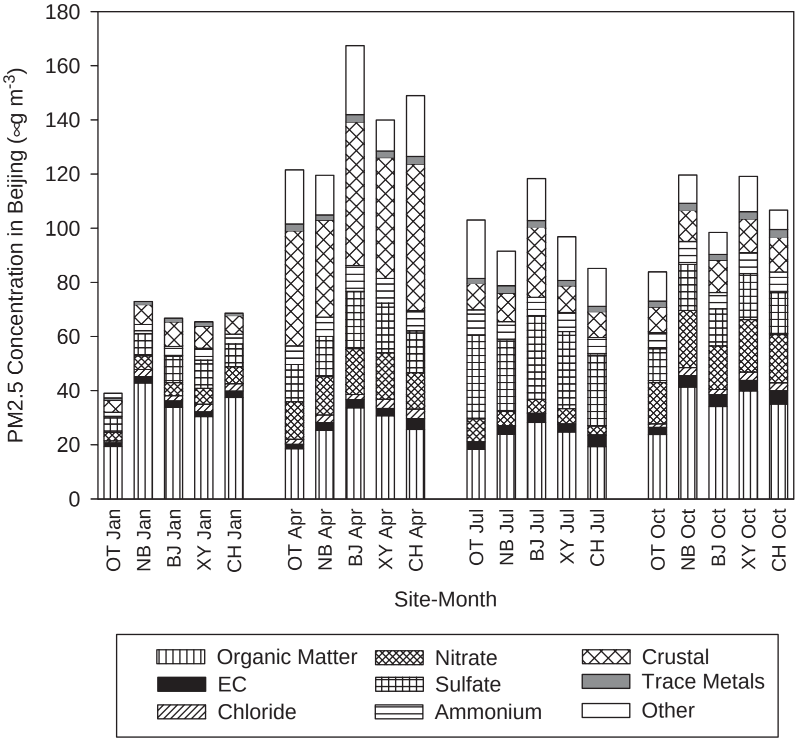

Fig. 1. Bulk composition of PM2.5 in Beijing. A factor of 1.4 is employed to convert OC to organic matter. Oxygen associated with crustal elements and trace metals have been accounted for (see Table S5 in Supplemental Materials).

that is all inorganic (Schauer, 2003). Thus the estimate of coal combustion based on the apportionment of OC in this study only includes low temperature coal combustion and does not include high combustion efficiency coal combustion processes, which are virtually all inorganic material. Dust is one of the major sources in April 2000, accounting for 22.5% of OC in PM2.5.

3.2. Fine particulate mass apportionment

Source contributions to PM2.5 mass can be calculated from the results of source apportionment of fine OC and the ratio of emissions of fine OC to fine particulate mass. The contributions from primary sources plus secondary ion concentrations including sulfate, nitrate, and ammonium explained 88% of PM2.5 mass on average (Table 2). The unexplained mass is likely dominated by uncounted primary sources including sources of inorganic aerosols such as low carbon fly ash from high efficiency coal combustion. The calculated major contributors to PM2.5 mass in Beijing in 2000 included dust (20±11%), secondary sulfate (17±7%), secondary nitrate (10±4%), coal combustion (7±5%), diesel and gasoline exhaust (7±3%), biomass aerosol (6±7%), secondary ammonium (6±1%), cigarette smoke (1±1%), and vegetative detritus (1±1%). The other organic matter was calculated by multiplying the other OC, defined by the difference between total OC and the sum of identified OC, by a factor of 1.4 to account for the mass of elements other than C in organic compounds. The 1.4 multiplier was used because it is more related to primary emissions and it is known that fossil fuel combustion is important in China.

In Beijing, large seasonal differences exist in fine particle source contributions. As seen in Fig. 2b, dust storms had a very large impact on Beijing aerosols in April 2000 accounting for 36% of fine particle mass. This influence was regional and independent of the site locations. Nine severe dust storm events occurred in Beijing during spring 2000 (He et al., 2001). Since the 24-h PM2.5 samples were collected on 6-day intervals and the samples for organic tracer study were monthly composites, it should be recognized that the high dust contributions in April were actually due to a severe dust event occurred on 25 April 2000 and a relatively mild event on 7 April 2000. It is interesting to note that dust contribution in July at BJ site is 39 $\mu g\,m^{-3}$, while it is only about 11 $\mu g\,m^{-3}$ at other sites. By examining the individual 24-h sample, it was found on 8 July 2000, Ca concentration at BJ site was extremely high (10.4 $\mu g\,m^{-3}$), which was even higher than the severe dust day on 25 April (ranging from 4.75 to 7.91 $\mu g\,m^{-3}$),

Table 1

Source contributions to fine organic carbon in PM2.5 in Beijing, China (mean + SE in μg m^{-3})

Site	Month	Diesel and gasoline exhaust	Vegetative detritus	Dust	Biomass aerosol	Coal combustion[a]	Cigarette smoke	Sum of identified sources	Measured organic carbon	R^2	χ^2	DF	% Mass explained
OT	January	3.56±0.48[b]	0.06±0.02	0.77±0.02	0.87±0.24	2.13±0.16		7.39±0.25	13.7±1.1	0.97	2.37	22	54
NB	January	3.26±0.49[b]	0.27±0.09	0.71±0.04	8.57±2.26	4.10±0.35	0.58±0.12	17.49±0.96	30.6±1.9	0.91	5.37	19	57
BJ	January	2.40±0.31[b]		1.75±0.04	3.51±0.96	3.34±0.26	0.58±0.10	11.58±0.47	24.2±1.6	0.97	3.02	21	48
XY	January	3.41±0.39[b]	0.20±0.08	1.57±0.04		2.69±0.21	0.79±0.13	8.66±0.21	21.6±1.4	0.96	3.67	28	40
CH	January	3.53±0.44[b]		1.01±0.03	8.77±2.28	3.79±0.31	0.47±0.10	17.57±1.05	26.7±1.8	0.96	3.02	20	66
OT	April	1.92±0.24[b]	0.22±0.04	4.00±0.02	0.34±0.10	1.05±0.09		7.54±0.12	13.2±1.1	1.00	3.49	25	57
NB	April	3.35±0.37	0.24±0.06	3.09±0.02	4.68±1.13	1.24±0.12	0.43±0.09	13.03±0.47	18.1±1.2	1.00	2.84	26	72
BJ	April	5.00±0.50[b]	0.17±0.08	4.78±0.03	3.02±0.82	2.11±0.19	0.83±0.14	15.90±0.41	23.9±1.7	1.00	2.34	27	66
XY	April	3.73±0.40[b]	0.28±0.11	3.98±0.02		1.67±0.14	1.20±0.19	10.86±0.21	21.9±1.5	1.00	2.91	27	50
CH	April	4.52±0.50	0.15±0.05	5.00±0.03	2.40±0.63	1.22±0.12	0.29±0.06	13.58±0.36	18.5±1.4	1.00	1.93	26	74
OT	July	2.39±0.28	0.17±0.06	1.46±0.04		0.52±0.05	0.48±0.10	5.02±0.17	13.1±1.0	0.97	3.63	23	38
NB	July	2.36±0.31	0.28±0.06	1.59±0.04		0.71±0.06	0.36±0.06	5.30±0.18	17.0±1.1	0.97	2.73	27	31
BJ	July	3.78±0.49	0.29±0.07	5.09±0.10		1.16±0.10	0.44±0.08	10.76±0.29	19.9±1.4	0.98	2.40	27	54
XY	July	2.91±0.34	0.40±0.11	1.38±0.05		0.77±0.07	1.00±0.16	6.46±0.21	17.6±1.2	0.96	3.06	27	37
CH	July	3.38±0.42	0.11±0.03	1.38±0.04		0.86±0.07	0.17±0.04	5.90±0.24	13.7±1.1	0.98	2.08	26	43n
OT	October	1.47±0.19	0.54±0.11	1.22±0.06	3.41±0.92	2.75±0.21	0.58±0.12	9.97±0.37	16.9±1.2	0.94	3.17	27	59
NB	October	6.12±0.71	0.88±0.19	1.26±0.09	18.98±4.63	4.07±0.38	1.23±0.23	32.54±1.92	30.7±1.8	0.93	2.88	28	106
BJ	October	7.12±0.67	0.48±0.13	1.84±0.07	11.21±2.78	2.42±0.25	1.03±0.18	24.10±1.12	24.3±1.7	0.97	2.83	27	99
XY	October	5.88±0.66	0.77±0.25	1.45±0.10	13.10±3.33	3.84±0.34	2.84±0.45	27.88±1.41	28.4±1.7	0.95	2.60	28	98
CH	October	7.20±0.69	0.49±0.12	1.75±0.07	3.02±0.82	2.58±0.22	0.82±0.15	15.86±0.49	24.9±1.9	0.97	2.69	27	64

[a] The coal contribution represents only high carbonaceous fly ash. See text for details.

[b] Diesel exhaust and gasoline exhaust are collinear.

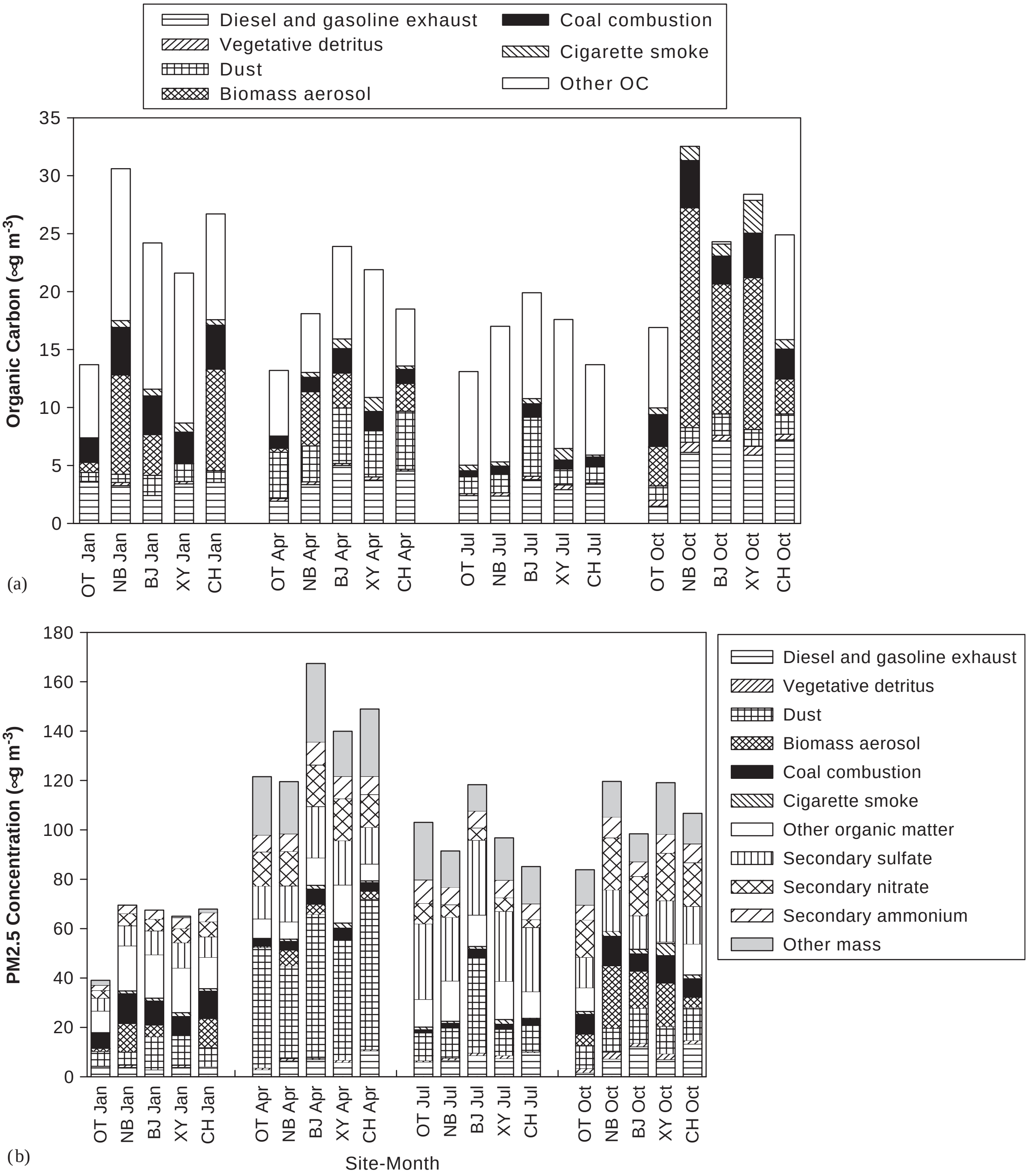

Fig. 2. (a) Source apportionment of fine OC in Beijing and (b) Primary and secondary sources of PM2.5 in Beijing. "Other mass" refers to the difference between the sum of identified sources and the measured PM2.5 concentration.

while it was only in the range of 0.38–0.87 μg m^{-3} at other sites on 8 July 2000. This suggests that this high contribution from dust in July at BJ site was indeed from local construction activities rather than long-range dust transport.

Dust concentrations determined by the CMB model were comparable to those estimated from the sum of the oxides of aluminum, silicon, calcium, iron, titanium, manganese, and potassium (correlation coefficient as 0.9881). In most cases, the CMB estimates tend to be

Table 2
Source contribution to PM2.5 mass concentrations in Beijing (μg m^{-3})

Site	Month	Diesel and gasoline exhaust	Vegetative detritus	Dust	Biomass aerosol	Coal combustion	Cigarette smoke	Other organic matter	Secondary sulfate	Secondary nitrate	Secondary ammonium	Other mass	Sum of identified sources	PM2.5 mass	% mass explained
OT	January	4.24	0.19	5.90	1.16	6.34		8.84	5.22	3.18	2.06	1.95	37.12	39.07	95
NB	January	3.89	0.83	5.44	11.44	12.20	0.93	18.36	8.16	4.98	3.28		69.50	69.35	100
BJ	January	2.86		13.40	4.69	9.94	0.93	17.68	9.66	4.78	3.57		67.50	63.27	107
XY	January	4.06	0.62	12.02		8.01	1.26	18.12	10.28	5.78	4.39	0.50	64.54	65.04	99
CH	January	4.21		7.73	11.71	11.28	0.75	12.79	8.27	6.19	3.65	1.31	66.58	67.89	98
Average	January	3.85	0.33	8.90	5.80	9.55	0.77	15.16	8.32	4.98	3.39	0.75	61.05	60.92	100
OT	April	2.96	0.68	48.82	0.45	3.13		7.94	13.42	13.77	6.82	23.55	97.98	121.53	81
NB	April	6.63	0.74	37.71	6.25	3.69	0.69	7.10	14.55	14.06	7.06	21.06	98.48	119.54	82
BJ	April	7.03	0.52	58.34	4.03	6.28	1.33	11.19	20.79	16.80	9.40	31.70	135.71	167.41	81
XY	April	5.93	0.86	48.57		4.97	1.92	15.46	18.02	16.97	9.06	18.19	121.77	139.96	87
CH	April	10.55	0.46	61.02	3.20	3.63	0.46	6.89	14.94	13.25	7.35	27.21	121.77	148.98	82
Average	April	6.62	0.65	50.89	2.79	4.34	0.88	9.72	16.34	14.97	7.94	24.34	115.14	139.48	83
OT	July	6.06	0.52	11.18		1.55	0.77	11.32	30.64	8.32	9.41	23.29	79.76	103.05	77
NB	July	6.75	0.86	12.17		2.11	0.58	16.39	25.83	5.09	7.10	14.61	76.89	91.50	84
BJ	July	8.72	0.90	38.97		3.45	0.70	12.80	30.33	5.03	6.80	10.62	107.71	118.33	91
XY	July	7.47	1.23	10.57		2.29	1.60	15.60	28.30	5.57	7.05	17.10	79.69	96.79	82
CH	July	9.88	0.34	10.57		2.56	0.27	10.92	25.98	3.22	6.37	15.02	70.12	85.14	82
Average	July	7.78	0.77	16.69		2.39	0.78	13.41	28.22	5.45	7.34	16.13	82.84	98.96	83
OT	October	1.75	1.67	9.34	4.55	8.18	0.93	9.71	12.35	15.15	5.99	14.26	69.63	83.89	83
NB	October	7.29	2.72	9.65	25.34	12.11	1.97		16.73	21.04	8.51	14.28	105.36	119.64	88
BJ	October	12.24	1.48	14.09	14.97	7.20	1.65	0.28	13.36	15.95	5.95	11.25	87.17	98.42	89
XY	October	7.01	2.38	11.10	17.49	11.43	4.54	0.73	16.74	19.24	7.69	20.80	98.34	119.14	83
CH	October	13.30	1.51	13.40	4.03	7.68	1.31	12.66	15.20	17.72	7.58	12.28	94.39	106.67	88
Average	October	8.32	1.95	11.52	13.28	9.32	2.08	4.68	14.88	17.82	7.14	14.57	90.98	105.55	86

Note: 1. The following factors are used to convert fine organic carbon to fine particulate mass: 0.304 for diesel exhaust, 0.839 for noncatalyst-equipped gasoline exhaust, 0.324 for vegetative detritus, 0.0819 for dust in April and 0.131 for dust in other seasons, 0.749 for biomass aerosol, 0.336 for coal combustion, 0.625 for cigarette smoke, and 0.714 for other organic matter. "Other mass" refers to the difference between PM2.5 mass and the sum of identified sources.

higher than those from the sum of oxides method (20% higher on average). This is probably due to the fact that the oxides method does not include all of the chemical components in the calculation. For example, the analysis of individual particles collected during dust storms occurring in spring 1995 and 1996 in Beijing showed 14.6% of the dust particles contained sulfur and 10.8% of dust particles contained nitrate (Zhang and Iwasaka, 1999).

Coal, wood, crop residues, and kerosene are commonly used in rural household while gaseous fuel, coal, and kerosene are the major fuels burned in urban household (Zhang et al., 2000). Coal is also the major fuel for industrial activities including providing heating in winter. Though the PM2.5 mass concentrations in January were the lowest, coal combustion contributed 16% of fine particle mass in January, higher than the levels in all other seasons (9% in October, 3% in April, and 2% in July). The low PM2.5 mass concentration was possibly due to the cold weather and frequent snow in Beijing in January. The snow would likely remove particles from the air, and also reduce the resuspension. Similar to coal combustion source, biomass aerosol contributed much more to fine particle mass in October (12%) and January (9%) compared to other seasons during calendar year 2000. However, it is an insignificant source of PM2.5 in July 2000 at all sites.

Diesel and gasoline exhaust in January is only about half ($3.85\,\mu g\,m^{-3}$) of the levels in other seasons. Frequent snow and cold temperature reduced outdoor activities and particle resuspension, leading to low vehicular emissions and particle concentrations in the atmosphere. Despite of the frequent and heavy snow in January, Chinese New Year is normally around January, thus traffic flow in Beijing is reduced significantly since it is the tradition that workers from other Provinces go back to their hometowns. In addition, fewer visitors come to Beijing during this cold and holiday season. Vegetative detritus shows the highest level in October ($1.95\,\mu g\,m^{-3}$), which is emitted to the atmosphere primarily by the way of wind abrasion of protrusions on the leaves.

The model results in Table 2 showed that diesel and gasoline exhaust had higher impact at two sites: BJ, a site surrounded by heavy traffic, and CH, a site close to a busy street. Though the XY site is located in central Beijing and also surrounded by heavy traffic, the impact of vehicular emissions is higher at the BJ site. The sum of hopanes and steranes is higher at the BJ site compared to the XY site in three out of four seasons, which also exhibits high correlation with OC (correlation coefficient as 0.9355). The level of dust contribution to fine OC was also slightly higher at BJ site, which was due to the active construction around Fourth Ring Road of Beijing in 2000. The significance of biomass aerosol at NB site can be consistently seen during all seasons except July, when biomass burning was insignificant at all sites. This suggested that it was primarily due to the local source influence. The increased importance of coal burning at the NB site indicated that at the site about 20 miles from central Beijing, coal burning practice, primarily from residential heating, became active during winter season as this site is characterized by light industrial activities. During all seasons, the highest level of cigarette smoke is always found in central Beijing (XY site), which is characterized by heavy traffic, plenty restaurants, and dense population.

It is important to note that application of local source profiles is the key for accurate CMB results. Uncertainty is inevitable when adopting some source profiles such as diesel and gasoline exhaust from the US in the present study.

4. Conclusions

Carbonaceous aerosol is one of the major constituents of PM2.5 with its mass percentage in PM2.5 increased up to 57% in winter. Up to six sources of OC in PM2.5, including diesel and gasoline exhaust, biomass aerosol, coal combustion, dust, vegetative detritus, and cigarette smoke, were identified with the chemical speciated results in combination with CMB analysis of fine particulate matter from five sites during four seasons in Beijing. These sources showed distinct seasonal trends. Coal combustion and biomass aerosol became important sources of OC in colder seasons, namely October and January, which accounted for 30% of OC in January and 50% of OC in October. As can be seen at all five sites, the highest PM2.5 mass concentration ($139\,\mu g\,m^{-3}$) was found in April, however, it is mainly attributed to dust ($51\,\mu g\,m^{-3}$ on average). The low level of fine particulate matter in January is possibly due to frequent snow and reduced activities in cold season. Though emission of diesel and gasoline exhaust is the lowest in January, but its contribution to PM2.5 is comparable to other seasons. Levoglucosan, a unique tracer for biomass burning, is not measured in any July samples, indicating that biomass burning is not active at this time in Beijing.

Acknowledgements

We thank the personnel from Peking University for the assistance in sampling, and Mr. Mark Mieritz of the Wisconsin State Hygiene laboratory for the assistance with the GC/MS analysis. We also wish to thank Paul Mayo at California Institute of Technology for helping to set up samplers in Beijing and for assisting with laboratory analyses at Caltech. XRF analyses were performed by the Desert Research Institute, Reno, NV.

Appendix A. Supplementary materials

The online version of this article contains additional supplementary data. Please visit doi:10.1016/j.atmosenv.2005.03.036

References

Bergin, M.H., Cass, G.R., Xu, J., Fang, C., Zeng, L.M., Yu, T., Salmon, L.G., Kiang, C.S., Tang, X.Y., Zhang, Y.H., Chameides, W.L., 2001. Aerosol radiative, physical, and chemical properties in Beijing during June 1999. Journal of Geophysical Research-Atmospheres 106, 17,969–17,980.

Birch, M.E., Cary, R.A., 1996. Elemental carbon-based methods for monitoring occupational exposures to particulate diesel exhaust. Aerosol Science and Technology 25, 221–241.

Cass, G.R., 1998. Organic molecular tracers for particulate air pollution sources. Trends in Analytical Chemistry 17, 356–366.

Chameides, W.L., Hu, H., Liu, S.C., Bergin, M., Zhou, X., Mearns, G., Wang, G., Kiang, C.S., Saylor, R.D., Luo, C., Huang, Y., Steiner, A., Giorgi, F., 1999. Case study of the effects of atmospheric aerosols and regional haze on agriculture: an opportunity to enhance crop yields in China through emission controls? Proceedings of the National Academy of Sciences 26, 13,626–13,633.

Chowdhury, Z., Hughes, L.S., Salmon, L.G., Cass, G.R., 2001. Atmospheric particle size and composition measurements to support light extinction calculations over the Indian Ocean. Journal of Geophysical Research-Atmospheres 106, 28,597–28,605.

Dan, M., Zhuang, G., Li, X., Tao, H., Zhuang, Y., 2004. The characteristics of carbonaceous species and their sources in PM2.5 in Beijing. Atmospheric Environment 38, 3443–3452.

Davis, B.L., Guo, J., 2000. Airborne particulate study in five cities of China. Atmospheric Environment 34, 2703–2711.

Environmental Protection Agency, 1987. Protocol for applying and validating the CMB model, EPA publication No. EPA-450/4-87-010, Research Triangle Park, NC, p. vii.

Frazier, M.P., Yue, Z.W., Tropp, R.J., Kohl, S.D., Chow, J.C., 2002. Molecular composition of organic fine particulate matter in Houston, TX. Atmospheric Environment 36, 5751–5758.

Hazenkamp-von Arx, M.E., Götschi, T., Ackermann-Liebrich, U., Bono, R., Burney, P., Cyrys, J., Jarvis, D., Lillienberg, L., Luczynska, C., Maldonado, J.A., Jaén, A., Marco, R., Mi, Y., Modig, L., Bayer-Oglesby, L., Payo, F., Soon, A., Sunyer, J., Villani, S., Weyler, J., Künzli, N., 2004. PM2.5 and NO_2 assessment in 21 European study centres of ECRHS II: annual means and seasonal differences. Atmospheric Environment 38, 1943–1953.

He, K., Yang, F., Ma, Y., Zhang, Q., Yao, X., Chan, C.K., Cadle, S., Chan, T., Mulawa, P., 2001. The characteristics of PM2.5 in Beijing, China. Atmospheric Environment 35, 4959–4970.

Hildemann, L.M., Markowski, G.R., Cass, G.R., 1991. Chemical composition of emissions from urban sources of fine organic aerosol. Environmental Science and Technology 25, 744–759.

Landis, M.S., Norris, G.A., Williams, R.W., Weinstein, J.P., 2001. Personal exposures to PM2.5 mass and trace elements in Baltimore, MD, USA. Atmospheric Environment 35, 6511–6524.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993. Sources of fine organic aerosol. 4. Particulate abrasion products from leaf surfaces of urban plants. Environmental Science and Technology 27, 2700–2711.

Salmon, L.G., Christoforou, C.S., Cass, G.R., 1994. Airborne pollutants in the Buddhist Cave Templates at the Yungang Grottoes, China. Environmental Science and Technology 28, 805–811.

Schauer, J.J., 2003. Evaluation of elemental carbon as a marker for diesel particulate matter. Journal of Exposure Analysis and Environmental Epidemiology 13, 443–453.

Schauer, J.J., Cass, G.R., 2000. Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers. Environmental Science and Technology 34, 1821–1832.

Schauer, J.J., Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., 1996. Source apportionment of airborne particulate matter using organic compounds as tracers. Atmospheric Environment 30, 3837–3855.

Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 1999. Measurement of emissions from air pollution sources. 2. C-1 through C-30 organic compounds from medium duty diesel trucks. Environmental Science and Technology 33, 1578–1587.

Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 2001. Measurement of emissions from air pollution sources. 3. C-1-C-29 organic compounds from fireplace combustion of wood. Environmental Science and Technology 35, 1716–1728.

Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 2002. Measurement of emissions from air pollution sources. 5. C-1-C-32 organic compounds from gasoline-powered motor vehicles. Environmental Science and Technology 36, 1169–1180.

Turpin, B.J., Saxena, P., Andrews, E., 2000. Measuring and simulating particulate organics in the atmosphere: problems and prospects. Atmospheric Environment 34, 2983–3013.

Wei, F., Teng, E., Wu, G., Hu, W., Wilson, W.E., Chapman, R.S., Pau, J.C., Zhang, J., 1999. Ambient concentrations and elemental compositions of PM10 and PM2.5 in four Chinese cities. Environmental Science and Technology 33, 4188–4193.

Wittig, A.E., Anderson, N., Khlystov, A.Y., Pandis, S.N., Davidson, C., Robinson, A.L., 2004. Pittsburgh air quality study overview. Atmospheric Environment 38, 3107–3125.

Zhang, D., Iwasaka, Y., 1999. Nitrate and sulfate in individual Asian dust-storm particles in Beijing, China in spring of 1995 and 1996. Atmospheric Environment 33, 3213–3223.

Zhang, J., Smith, K.R., Ma, Y., Ye, S., Jiang, F., Qi, W., Liu, P., Khalil, M.A.K., Rasmussen, R.A., Thorneloe, S.A., 2000. Greenhouse gases and other airborne pollutants from household stoves in China: a database for emission factors. Atmospheric Environment 34, 4537–4549.

Zheng, M., Cass, G.R., Schauer, J.J., Edgerton, E.S., 2002. Source apportionment of PM2.5 in the Southeastern United States using solvent-extractable organic compounds as tracers. Environmental Science and Technology 36, 2361–2371.