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## The characteristics of PM<sub>2.5</sub> in Beijing, China

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### Abstract

Weekly PM<sub>2.5</sub> samples were simultaneously collected at a residential (Tsinghua University) and a downtown (Chegongzhuang) site in Beijing from July 1999 through September 2000. The ambient mass concentration and chemical composition of the PM<sub>2.5</sub> were determined. Analyses included elemental composition, water-soluble ions, and organic and elemental carbon. Weekly PM<sub>2.5</sub> mass concentrations ranged from 37 to 357 µg/m<sup>3</sup>, with little difference found between the two sites. Seasonal variation of PM<sub>2.5</sub> concentrations was significant, with the highest concentration in the winter and the lowest in the summer. Spring dust storms had a strong impact on the PM<sub>2.5</sub>. Overall, organic carbon was the most abundant species, constituting no less than 30% of the total PM<sub>2.5</sub> mass at both sites. Concentrations of organic and elemental carbon were 35% and 16% higher at Tsinghua University than at Chegongzhuang. Ammonium, nitrate and sulfate were comparable at the sites, accounting for 25–30% of the PM<sub>2.5</sub> mass. © 2001 Elsevier Science Ltd. All rights reserved.

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### 1. Introduction

The combination of high population density and rapid industrialization in China has inevitably led to an increase in emissions. These emissions have exacerbated the air pollution problems in large and medium size cities resulting in visibility reduction and health concerns. Ambient aerosols are largely responsible for the visibility deterioration seen in different areas (Chan et al., 1997; Christoforou et al., 2000). The health impact of particles has come into question due to epidemiological studies reporting an association between fine particle concentration and hospital admission records (IIASA, 2000a,b; WHO Regional Office For Europe; UN

Economic Commission For Europe, 1999). It has also been suggested that aerosols reduce agricultural crop yields due to reduced sunlight.

Relatively little data is available on fine particle concentrations or their composition in China. Winchester studied PM<sub>2.0</sub> at the Great Wall near Beijing in the late 1970s and found comparable elemental profiles to background aerosols in remote areas of the world (Winchester et al., 1981). A great deal of change has taken place since then and ambient particulate sampling studies have been conducted in a variety of cities. For instance, the urban air quality in Wuhan in the 1980s was shown to have an impact on the pulmonary function in children (He et al., 1993) and a local smelter was identified as the primary source of PM (Zelenka et al., 1994). A study in a coal mining region at Yungang demonstrated the local transport and dry deposition of carbonaceous particles (Christoforou et al., 1994). More

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recently, a study in Dongying, Jinan, Qingdao, Beijing and Shanghai showed that most of the ambient particle mass was in the submicron size range (Davis and Guo, 2000). A joint study sponsored by the USEPA (Wei et al., 1999) determined the concentration of  $PM_{10}$  and fine particles in Lanzhou, Chongqing, Wuhan, and Guangzhou. The common finding from these studies is that the ambient aerosol concentration in these cities are generally in the  $100\text{--}500\ \mu\text{g}/\text{m}^3$  range with the highest concentration in the winter months.

The first comprehensive study on  $PM_{2.5}$  in Beijing was done in 1989–1990 (Chen et al., 1994). The average concentration of  $PM_{2.5}$  for four seasons was reported to be in the  $70\text{--}90\ \mu\text{g}/\text{m}^3$  range. An average organic carbon (OC) to elemental carbon (EC) ratio of 1.1 was reported. The composition of  $PM_{2.5}$  was found to have high sulfur content, and heavy duty diesel exhaust and re-entrained road dust were identified as major sources by CMB analysis. An earlier study by Su et al. (1989) also pointed out the significance of carbonaceous soot and sulfate aerosols in Beijing and adjacent cities. Most recently, Zhang and Friedlander (2000) reviewed the published literature on ambient PM studies in Beijing over the last 15 years. A species profile was assembled from several studies and compared to that in Los Angeles. Some elemental species, most notably silicon, were found to be an order of magnitude higher than in Los Angeles.

Coal burning has been identified as a major source of  $PM_{2.5}$  in China. Coal is used both industrially and domestically. The domestic use of coal and biomass as a household fuel can also cause serious indoor air quality problems in poorly ventilated dwellings (Yan, 1989; Lan et al., 1993; Florig, 1997). Concern over emissions from mobile sources has been growing along with the vehicle population. For example the vehicle population in Beijing grew at a rate of 15% per year through the 1990s, and now exceeds 1.3 million vehicles. Emissions from vehicles built in China before 1999 were uncontrolled.

Air quality concerns has led to the adoption of a large number of control measures for PM. New or expanded power plants or industrial boilers must use sulfur and PM abatement equipment. Cities are encouraged to replace individual household coal heating stoves with centralized district heat. Use of lump coal is being phased out and incentives are in place to encourage the use of low-sulfur, low-ash coal or to convert to cleaner fuels such as natural gas or liquefied petroleum gas. New vehicles must meet the Euro I emission standards, and some cities, such as Beijing, have adopted Euro II standards. Emission control retrofit programs are in place in some areas. In Beijing, diesel buses are being converted to use compressed natural gas. Steps are also required to reduce dust from construction areas, including the encouragement of more green areas.

At this time, China has a  $PM_{10}$  standard, but does not have one for  $PM_{2.5}$ . Therefore, no  $PM_{2.5}$  monitoring is in place. The purpose of this study was to initiate  $PM_{2.5}$  monitoring in Beijing. The composition of the PM was also determined since this provides useful information in regards to PM sources. One week integrated  $PM_{2.5}$  measurements were made for over a year starting in June 1999. The paper will summarize the major findings for  $PM_{2.5}$  in Beijing with a focus on seasonal changes. This information will provide an essential baseline to examine the impact of environmental changes in the transportation, energy, and land use sectors.

## 2. Experimental

Sampling was conducted at two sampling sites in Beijing; one located on the campus of Tsinghua University in a residential area, and one downtown at an air quality monitoring station at Chegongzhuang (see Fig. 1). The distance between the two sites is about 10 km. The Chegongzhuang site is located near the second ring road, a major thoroughfare.  $PM_{10}$  and gaseous concentrations of carbon monoxide, sulfur dioxide, nitrogen oxides and ozone were determined for the same sampling period at the Chegongzhuang site.

Beijing is the capital of China, with a population of over 11 million. It is located at the northwestern border of the Great North China Plain at  $39^{\circ}48'N$  latitude and  $116^{\circ}28'E$  longitude at an altitude of 44 m above mean sea level. Mongolia is to the north of Beijing, the Gobi desert is approximately 400 km to the northwest, the Yanshan Mountain range is to the northeast, and the

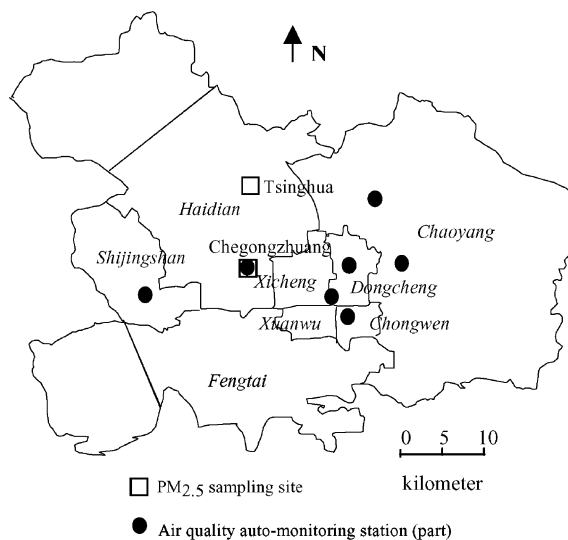


Fig. 1. Beijing airshed and the  $PM_{2.5}$  sampling sites.

Bohai Sea is 160 km to the southeast. In Beijing, criteria pollutants such as sulfur dioxide, carbon monoxide,  $\text{NO}_x$  and  $\text{PM}_{10}$  are monitored daily at air sampling stations, including the downtown site in Chegongzhuang.

### 2.1. Sampling system

A low-flow rate sampler, LFS (Aerosol Dynamics Inc., Berkeley, CA) was deployed at each site to collect airborne  $\text{PM}_{2.5}$ . The two samplers were placed on the roofs of 3 m tall buildings, resulting in an effective inlet height above the ground of about 4.5 m. The LFS has three parallel sampling inlets for the collection of  $\text{PM}_{2.5}$  samples. Each filter cassette has an impaction plate coated with oil to prevent particle bounce. As shown in Fig. 2, the three parallel sampling trains of the LFS are:

1. an inorganic species cassette with a Teflon impactor followed by a glass denuder. The glass denuder is coated with a 2% carbonate solution prepared in 50/50 water–methanol to remove the acidic gases. The coated denuder removes nitric acid, which can be recovered and measured, although this was not done in this study. Nitric acid volatilized from the Teflon filter is collected on the nylon filter. Hence the reported particulate nitrate is the sum of nitrate on both the Teflon and nylon filters. Water soluble ions are determined from this Teflon filter. Mass can be

determined from this filter as well and compared to that from the single-filter cassette for quality assurance purposes. Teflon filters were Gelman (Ann Arbor, MI) PTFE Teflon-membrane 47 mm diameter filters (Teflon™ #R2PJ047) with a 2  $\mu\text{m}$  pore size. Nylon filters were Gelman (Ann Arbor, MI), 1  $\mu\text{m}$  pore size, 47 mm diameter nylon membrane filters (#66509).

2. A single-filter  $\text{PM}_{2.5}$  cassette consists of an aluminum impactor followed by a single Teflon filter. This filter was used to determine  $\text{PM}_{2.5}$  mass and for elemental analysis.
3. A tandem-filter  $\text{PM}_{2.5}$  cassette accommodates two Gelman (Ann Arbor, MI) quartz-fiber filters (#2500 QAT-UP) for carbon analysis. These filters were pre-fired at 900°C for a minimum of 3 h to remove any carbon.

The critical orifices inside these sampling cassettes provide a constant airflow through each sampling train and serve to protect the rotameters. The vacuum pump draws air through each filter cassette at a flow rate of 0.41/min.

### 2.2. Chemical analysis

The samples on the denuded Teflon-membrane filter were analyzed for mass by gravimetry and for water-soluble ions (sulfate, nitrate, chloride, ammonium,

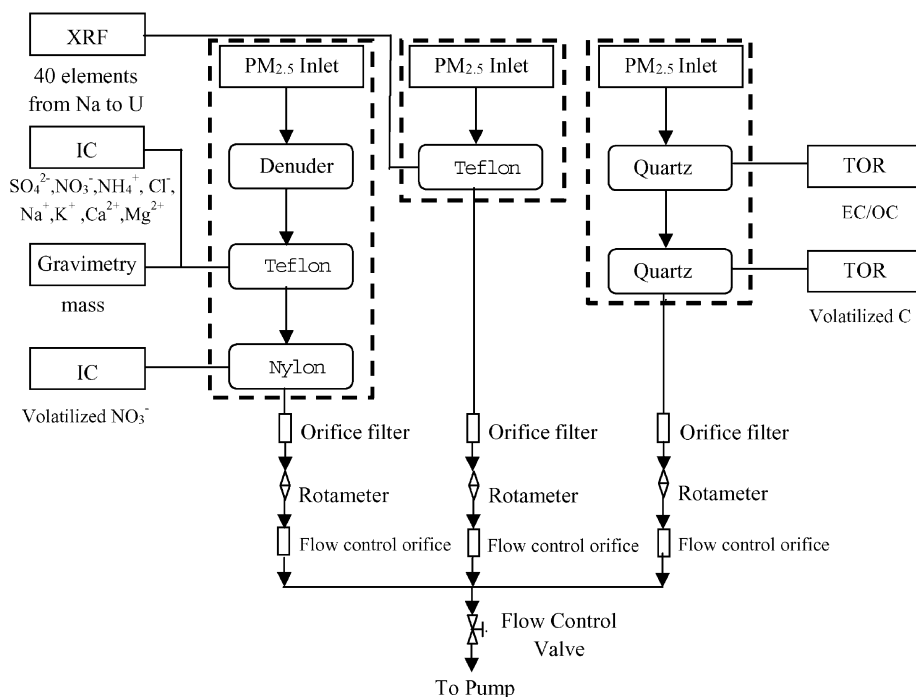


Fig. 2. Flow diagram for  $\text{PM}_{2.5}$  low-flow rate sampler.

sodium, potassium, magnesium and calcium) by ion chromatography (IC), while the nylon back filter was analyzed for chloride, nitrate, and sulfate ions. The IC analyses were conducted at the Hong Kong University of Science and Technology. The Teflon-membrane filter of the single-filter PM<sub>2.5</sub> cassette was analyzed for mass by gravimetry and for 40 elements (from aluminum to uranium) by X-ray fluorescence (XRF) using standard methods (Chow and Watson, 1994). The front quartz filter of the tandem-filter PM<sub>2.5</sub> cassette was analyzed for OC and EC by the thermal/optical reflectance (TOR) method (Chow et al., 1993). A subset of the backup quartz filters was also analyzed for volatilized/adsorbed carbon. OC and EC remain operational definitions. The XRF and OC/EC analyses were performed at the Desert Research Institute in Reno, NV. While the TOR method employed in this study is commonly used for PM measurements, it should be recognized that other methods of determining the OC and EC fractions could give different results. The 1-week sampling periods exacerbate the possible loss of semi-volatile organic compounds during sampling.

Table 1 presents the uncertainties in the measurements for the Chegongzhuang site. The uncertainties for the

Tsinghua site were essentially the same. Measurements of phosphorous, arsenic, titanium and chromium were within the uncertainty of the measurement and hence will not be reported.

### 2.3. Quality control

Prior to the start of the 52-week study, parallel sampling was conducted for 5 weeks with two LFS at the same site. Gravimetric analysis of the parallel samples was conducted both in Beijing and the USA, and agreeable results ( $\pm 5\%$ ) were acquired. Background contamination was routinely (once for each batch of eight sets of samples) monitored with operational blanks (unexposed filters), which were processed simultaneously with field samples.

Problems were experienced in filter weighing during the first summer of the study (7 July–24 September 1999). Therefore, no mass data is provided for this period. Because of this, mass measurements were extended through the second summer. Speciation of the collected mass, however, was only performed on the samples collected during the first summer.

Comparison of filter mass from the two Teflon filters collected simultaneously on a single sampler showed poor agreement at times, suggesting that there were some additional weighing problems. It is unlikely that this was due to sampler flow problems since comparison of XRF sulfur to the water soluble sulfate sulfur on the same two filters showed reasonable agreement. This is shown in Fig. 3, where it is seen that the slope of the linear regression is 0.86 and the correlation coefficient is 0.79 at the Chegongzhuang site. At the Tsinghua site, the slope was 0.76 with a correlation coefficient of 0.52. Sulfur dioxide in the sample stream can be adsorbed by nylon filters, resulting in water soluble sulfate. However, the carbonate denuders used to remove nitric acid should remove sulfur dioxide from the sample in the LFS. The efficiency of these denuders for sulfur dioxide has not been determined. However, if it is assumed that they were highly efficient, then any sulfate found on the nylon filter could be attributed to leaks past the Teflon filter. When the sum of the sulfate on the Teflon and nylon filters was compared to the XRF sulfur, the linear correlation improved, as shown in Fig. 4. The slopes of the regressions were 0.90 at both sites, with regression coefficients of 0.89 and 0.81 strongly suggesting that this did account for leaks. Total chloride determined by XRF was also compared to the IC soluble chloride. The linear regression slopes were 0.74 and 0.49 for the Chegongzhuang and Tsinghua sites, with correlation coefficients of 0.75 and 0.49, respectively. These correlations included all samples, and could not be corrected for any filter leaks due to high chloride blanks on the nylon filters. Since the efficiency of the denuders for sulfur dioxide has not been proven, and the average

Table 1  
Uncertainties in the chemical measurements at the Chegongzhuang site

Species	Conc. ( $\mu\text{g}/\text{m}^3$ )
NO <sub>3</sub> <sup>-</sup>	0.01
SO <sub>4</sub> <sup>2-</sup>	0.01
NH <sub>4</sub> <sup>+</sup>	0.01
K <sup>+</sup>	0.02
OC	0.8
EC	0.8
Na	0.162
Mg	0.069
Al	0.034
Si	0.033
S	0.033
Cl	0.087
K	0.029
Ca	0.023
Mg	0.069
Mn	0.004
Fe	0.009
Ni	0.002
Cu	0.002
Zn	0.004
Se	0.003
Br	0.003
Pb	0.007
P	0.039
As	0.049
Ti	0.093
Cr	0.011

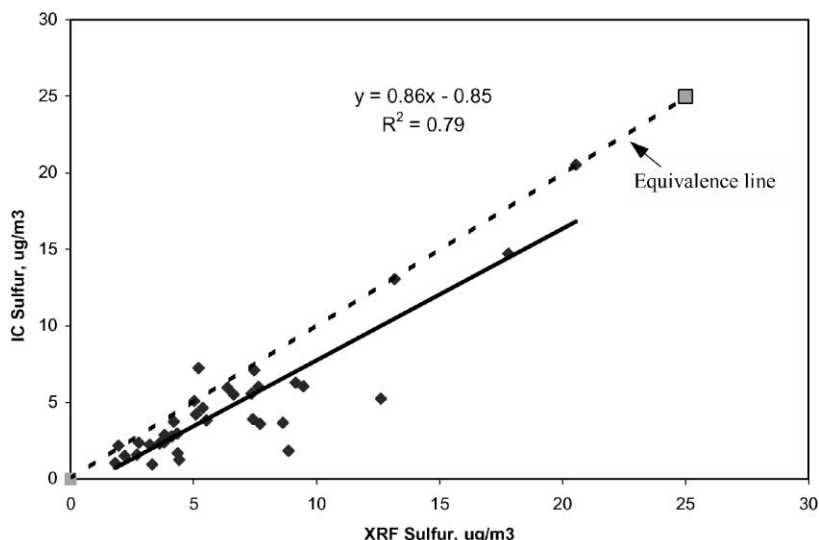


Fig. 3. Comparison of water soluble sulfate sulfur determined by IC and total sulfur determined by XRF at the Chegongzhuang site.

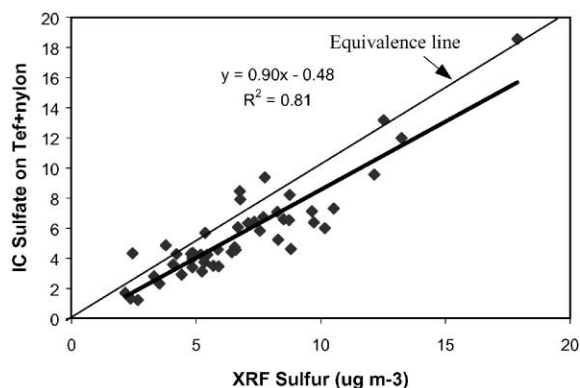


Fig. 4. Comparison of the sum of Teflon and Nylon water soluble sulfate sulfur with total sulfur determined by XRF.

sulfate correction is modest, the sulfate results reported in this paper are for the Teflon filter only.

### 3. Results and discussion

#### 3.1. $PM_{2.5}$ mass concentrations

The sample-to-sample and site-to-site variations in weekly average  $PM_{2.5}$  mass concentrations are shown in Fig. 5. Weekly  $PM_{2.5}$  concentrations ranged from 37 to 357  $\mu\text{g}/\text{m}^3$ , with modest differences between the two sites. The largest differences were for the April–July period, when the Chegongzhuang site consistently had lower mass than the Tsinghua site. The annual average

$PM_{2.5}$  mass concentration was 115 and 127  $\mu\text{g}/\text{m}^3$  at the Chegongzhuang and Tsinghua sites, respectively. As noted above, the distance between the two sites was about 10 km. Given the similarity in the data, it appears that the proximity of the downtown site to the second ring road was not a major factor.

Strong temporal variations in  $PM_{2.5}$  mass concentrations were observed at the two sites. The data was examined for seasonal trends, with the seasons defined as follows: Autumn—September–October; Winter—November–March; Spring—March–May; and Summer—June–August. Several severe  $PM_{2.5}$  episodes occurred in the winter. Variations in the weekly average  $PM_{2.5}$  were as high as a factor of 2.5 for consecutive weeks.

As illustrated in Fig. 5,  $PM_{2.5}$  concentrations were highest during the winter, decreased through the spring, and tended to be lowest during late spring, summer, and early autumn. At the Chegongzhuang site, the  $PM_{2.5}$  mass averaged 176  $\mu\text{g}/\text{m}^3$  during winter, exceeding the 115  $\mu\text{g}/\text{m}^3$  annual average by 53%. The fall, spring and summer averages were 112, 89 and 76  $\mu\text{g}/\text{m}^3$ , respectively.

The winter  $PM_{2.5}$  mass concentration peak is most likely due to a combination of increased emissions from heating sources coupled with meteorological conditions that limits dispersion. About 23% of the annual coal consumption in Beijing is used for residential heating (UNEP and WHO, 1992). Since the emissions from residential heating are emitted near ground level, and are likely to be higher per unit mass of coal than for boilers, their contribution to the winter  $PM_{2.5}$  is likely to be significant.

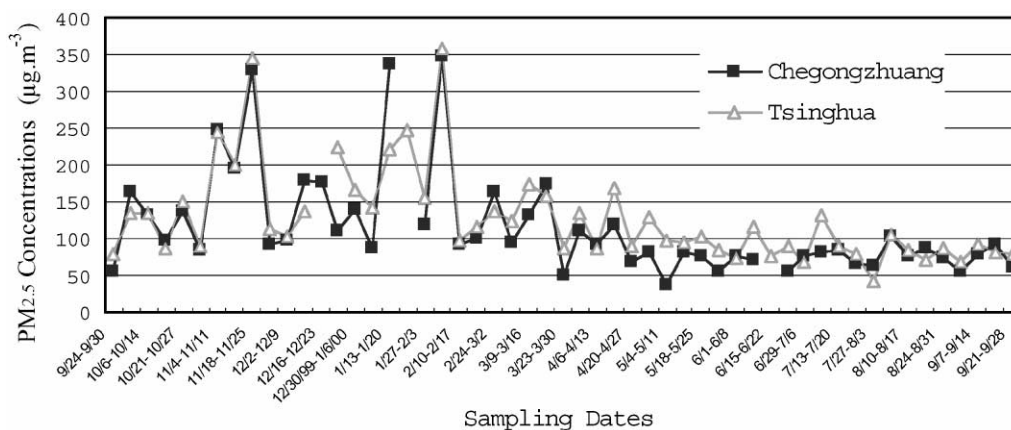


Fig. 5. Variations of weekly  $PM_{2.5}$  mass with time between 24 September 1999 and 28 September 2000 at the two Beijing sites.

At the Chegongzhuang site, weekly average  $PM_{2.5}$  constituted 43–89% of  $PM_{10}$  mass, which was monitored continuously with a tapered element oscillating microbalance (TEOM). The average  $PM_{2.5}/PM_{10}$  ratio was 0.64, indicating that  $PM_{2.5}$  contributes significantly to  $PM_{10}$ . This ratio is comparable with those measured in three southern Chinese cities, i.e. Guangzhou, Chongqing and Wuhan (Wei et al., 1999). An analysis of several of the weekly average highest  $PM_{2.5}$  concentration periods suggested that high  $PM_{2.5}$  concentrations are frequently associated with elevated  $PM_{10}$ .

### 3.2. $PM_{2.5}$ chemical composition

Table 2 compares the concentrations of all the measured species at the two sites averaged over the entire sampling period. Generally, the average concentrations are very similar, indicating that the  $PM_{2.5}$  is not being strongly influenced by local sources. The exception to this may be OC, which averaged 35% higher at the Tsinghua site than the Chegongzhuang site. Elemental carbon was 16% higher at the Tsinghua site. Hence the OC/EC ratio increased from 2.47 at the Chegongzhuang site to 2.88 at the Tsinghua site. This may be due to the presence of nearby restaurants. Of the remaining species, sodium, magnesium and selenium have the highest potential for error since their average concentrations were only three times higher than their average uncertainty.

#### 3.2.1. Seasonal averages

Table 3 lists the maximum and the average weekly concentrations of  $PM_{2.5}$  and its chemical constituents by season at the Chegongzhuang site. The particulate nitrate mass is that measured on the Teflon membrane filters plus that on the nylon backup filters. OC

Table 2  
Average concentrations (in  $\mu\text{g}/\text{m}^3$ ) at the two Beijing sites

Species	Chegongzhuang	Tsinghua	Ratio
$\text{NO}_3^-$	10.3	9.9	0.96
$\text{SO}_4^{2-}$	14.47	14.08	0.97
$\text{NH}_4^+$	6.22	6.51	1.05
$\text{K}^+$	2.22	2.21	1.00
OC	21.5	29.1	1.35
EC	8.7	10.1	1.16
Na	0.42	0.41	0.98
Mg	0.22	0.22	1.00
Al	0.8	0.8	1.00
Si	2.39	2.46	1.03
S	6.57	6.93	1.05
Cl	2.05	2.45	1.20
K	2.83	3.05	1.08
Ca	1.23	1.21	0.98
Mn	0.097	0.093	0.96
Fe	1.14	1.13	0.99
Ni	0.015	0.012	0.80
Cu	0.035	0.039	1.11
Zn	0.48	0.57	1.19
Se	0.009	0.01	1.11
Br	0.017	0.023	1.35
Pb	0.304	0.335	1.10

measurements on the front quartz-fiber filters may possess a positive bias owing to adsorption of organic gases (positive artifact), but the OC measured on the backup quartz-fiber filter may overestimate this artifact in many cases (Chow et al., 1996). Therefore, the OC results reported in this paper are uncorrected, i.e. for the front quartz-fiber filter only.

As noted above, mass data is not available for the 1999 summer period. It can, however, be estimated from

Table 3  
Statistical summary of weekly PM<sub>2.5</sub> measurements (in µg/m<sup>3</sup>) at the Chegongzhuang site

	Summer		Fall		Winter		Spring	
	Average	Max.	Average	Max.	Average	Max.	Average	Max.
Mass	ND <sup>a</sup>	ND	111.6	162.6	175.9	347.1	88.6	172.9
NO <sub>3</sub> <sup>-</sup>	4.59	17.8	11.16	17.41	15.35	53.96	7.26	20.15
SO <sub>4</sub> <sup>2-</sup>	17.14	27.03	12.55	22.81	24.87	81.36	10.15	19.15
NH <sub>4</sub> <sup>+</sup>	5.70	8.45	4.91	8.43	7.80	21.86	4.28	12.15
K <sup>+</sup>	2.31	3.59	2.57	4.26	2.55	8.13	1.30	2.48
OC	13.42	18.12	28.79	35.91	31.49	58.92	18.21	28.13
EC	6.27	12.04	10.23	12.31	11.08	25.40	6.67	13.93
Al	0.44	0.81	0.73	1.21	0.74	1.56	1.37	5.28
Si	1.24	2.08	2.35	3.61	2.24	4.50	4.08	16.19
P	0.016	0.034	0.04	0.06	0.08	0.16	0.01	0.06
S	6.76	14.06	4.92	7.46	8.15	20.54	4.40	7.36
Cl	0.05	0.20	1.25	2.18	4.61	10.04	0.87	3.91
K	2.21	3.54	3.21	3.97	3.24	7.53	2.57	4.23
Ca	0.924	1.824	1.55	1.77	1.05	2.02	1.71	6.25
Mg	0.15	0.25	0.26	0.35	0.19	0.37	0.31	0.97
Mn	0.075	0.097	0.14	0.22	0.10	0.26	0.09	0.16
Fe	0.76	1.09	1.32	1.66	1.17	2.58	1.52	5.22
Ni	0.009	0.019	0.001	0.002	0.003	0.009	0.004	0.007
Cu	0.022	0.044	0.032	0.043	0.051	0.119	0.028	0.041
Zn	0.343	0.558	0.511	0.745	0.612	1.500	0.425	0.697
Se	0.008	0.014	0.008	0.012	0.012	0.026	0.005	0.009
Br	0.011	0.028	0.021	0.036	0.018	0.062	0.021	0.031
Pb	0.22	0.38	0.28	0.45	0.40	1.20	0.26	0.41
n <sup>b</sup>	12		6		17		13	

<sup>a</sup>ND= not determined.

<sup>b</sup>n = number of samples.

the sum of species using correction factors to account for the hydrogen and oxygen estimated to be associated with OC and the oxygen associated with elements assumed to be present as oxides. On this basis, the average and maximum summer mass was 59.5 and 96.7 µg/m<sup>3</sup> at the Chegongzhuang site, respectively. Below it is shown that the sum of the measured species accounted for approximately 80% of the observed mass for the fall, winter and spring periods. Assuming that was true for the 1999 summer period as well, then the mass is estimated to be 74 and 121 µg/m<sup>3</sup>, for the average and maximum, respectively. Note that the average estimated PM<sub>2.5</sub> mass concentration is very close to the 76 µg/m<sup>3</sup> measured in the summer of 2000. Since the 1999 summer mass is an estimate, the percent contributions to the observed mass will not be discussed for the summer.

The greatest contributors to the PM<sub>2.5</sub> mass (generally > 1 µg/m<sup>3</sup>) were chloride, nitrate, sulfate, ammonium, OC, EC, silicon, potassium, calcium, and iron. On average, OC was the most abundant species, ranging from 17.9% to 25.7% of the average seasonal mass. OC had a maximum concentration of 58.9 µg/m<sup>3</sup> at the

Chegongzhuang site during the week from 18 to 25 November 1999. For this period, sulfate was actually the most abundant species with a concentration of 62.4 µg/m<sup>3</sup>. Total carbon (TC, also termed carbonaceous aerosol, is the sum of the OC and EC) constituted 12–69% and averaged 30% of PM<sub>2.5</sub> mass for 1-week integrated samples. The seasonal average OC/EC ratios were 2.81, 2.84, 2.73 and 2.14 for fall, winter, spring and summer, respectively. This is a much higher ratio than the 0.5–0.6 reported by Dod et al. (1986) for samples analyzed by evolved gas analysis. Some of the difference may be due to the analytical methods used. For example, Chow et al. (2001) recently compared two thermal evolution methods that use different temperature and optical monitoring protocols. A factor of two difference was seen for elemental carbon in ambient samples.

Concentrations of particulate nitrate, sulfate, and ammonium were much higher in winter than in fall and spring, whereas concentrations of OC and EC were similar in the fall and winter. On the other hand, the sum of the ammonium, nitrate, and sulfate ions accounted for 25.6%, 27.3% and 24.5% of the seasonal average

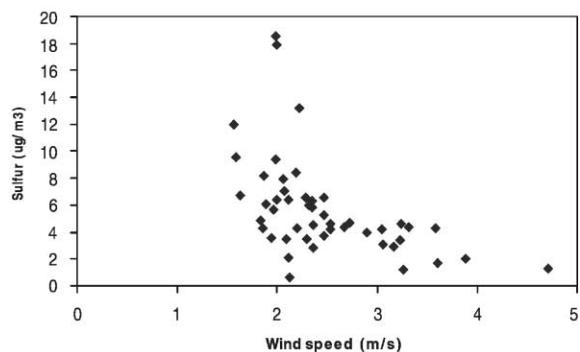


Fig. 6. Relationship between average wind speed and total particulate sulfur.

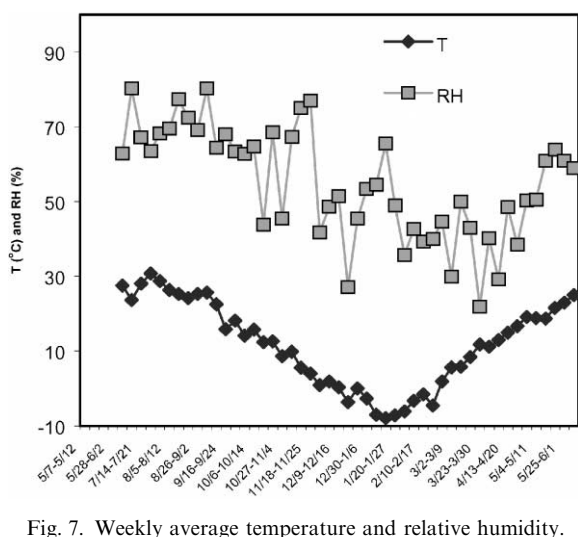


Fig. 7. Weekly average temperature and relative humidity.

mass for fall, winter and spring, respectively. The abundance of sulfate in winter could be related to high concentrations of  $\text{SO}_2$ , which are likely due to increased coal consumption during heating period combined with poor dispersion. The latter is supported by the fact that total particulate sulfur, as determined by XRF, generally decreased with increasing wind speed (Fig. 6). In 1999, the average ambient concentration of  $\text{SO}_2$  in winter was 12.5 and 4.7 times those in summer and autumn, respectively. For nitrate species, the low temperature ( $<15^\circ\text{C}$ ) in late fall and winter, as shown in Fig. 7, favors a shift from the gas phase as nitric acid ( $\text{HNO}_3$ ) to the particle phase as ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) (US EPA, 1999). In this regard, note that the nitrate was lowest during the summer.

The seasonal average molar ratios of ammonium to sulfate were 2.09, 1.67, 2.26, and 1.78 for fall–summer, respectively. Hence there was sufficient ammonium ion present in the samples to assume that the sulfate is

present as ammonium sulfate for the fall and spring seasons. This, however, ignores the nitrate, which was also abundant. The amount of nitrate present on the nylon filters was 47%, 23%, 19%, and 20% for the summer, fall, winter, and spring seasons, respectively. This nitrate is due to the volatilization of ammonium nitrate from the first filter. The ammonia associated with this nitrate is not captured, and thus is not included in the ammonium results in Table 3. The average over all four seasons for the missing ammonium is  $0.7 \mu\text{g}/\text{m}^3$ . If this ammonium is included, then these samples had sufficient ammonium ion to account for 72%, 63%, 81% and 82% of the nitrate and sulfate for the fall–summer, respectively.

While the  $\text{PM}_{2.5}$  mass decreased going from winter to spring, the concentrations of crustal species such as aluminum, iron, silicon, calcium and magnesium increased. The spring to winter average concentration ratios for these species were 1.86, 1.30, 1.82, 1.62 and 1.63, respectively. The spring maximum weekly concentration of silicon was  $16.2 \mu\text{g}/\text{m}^3$ , which exceeded the maximum value in winter by a factor of 3.6. This was probably due to frequent dust storms, which impacted Beijing nine times in the spring of 2000. The frequency and severity of the storms were the worst in 50 years.

Calcium has been used as an indicator element for construction dust in Beijing. This is supported by the work of Zhang and Iwasaka (1999) who used EDX to analyze the elemental compositions of individual particles collected during five dust storms in the spring of 1995 and 1996. Most of the particles were irregularly shaped and contained Si, Al, Mg, K, Ca, and Fe. They also found that Ca abundant particles with little or no other mineral elements existed in all samples. They concluded that the Ca abundant particles originated from local construction activities. Fig. 8 shows the Ca/Si and Ca/Al ratios for this study for both sites. The ratios are the lowest during the winter period when construction activity has decreased. The increase in elemental concentrations during the spring weekly maximum was examined since this was impacted by dust storms. The spring maximum weekly concentrations of aluminum, silicon, iron, calcium and magnesium were factors of 7.15, 7.22, 4.47, 5.93, and 5.10 higher than the winter weekly average concentration, suggesting that the impact by long range transport of particles generated in dust storms as well as by locally generated dust. On the other hand, the concentrations of trace elements such as copper, zinc, selenium, and lead were not impacted by the dust storms. Overall, it was found that the ratio of Ca/Si significantly decreased in samples collected during dust storms. Thus, it is concluded that this data is consistent with construction activity being a significant Ca source.

High abundances of total and soluble potassium are present. The ratio of total potassium to water soluble



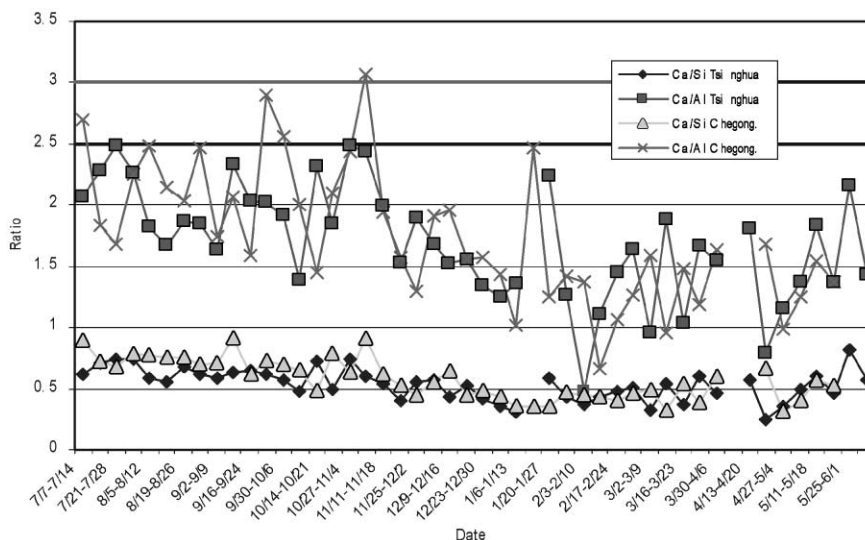


Fig. 8. Ca/Si and Ca/Al ratios at the two Beijing sites.

potassium was 0.96, 1.25, 1.27 and 1.98 for the summer–spring seasons, respectively. Of all source emissions, biomass burning has the highest abundance of both total potassium and soluble potassium (Watson and Chow, 1998). A study on source profiles for the fine PM size fraction in Tianjin, a large urban area located approximately 140 km southeast of Beijing, showed an enrichment of potassium for the coal burning profile (Zelenka et al., 1994). They concluded that this phenomenon was probably due to the practice of burning vegetative scrap along with the coal. Around Beijing, biomass burning is widely present and undoubtedly contributes to the high abundance of water-soluble potassium, which is expected to peak in the mid October to mid November time. The impact of biomass burning needs further investigation.

Several of the elements in Table 3 such as manganese, nickel, copper, zinc, selenium, and lead, are often classified as toxic. Of these, only lead has a national ambient air quality standard in China. The  $1.5 \mu\text{g}/\text{m}^3$  quarterly average standard for lead in TSP (total suspended particulate matter, i.e. particulate matter with aerodynamic diameters less than  $100 \mu\text{m}$ ) was never approached even by the maximum concentration for a single weekly  $\text{PM}_{2.5}$  sample. In addition, annual average concentration of lead in  $\text{PM}_{2.5}$  was  $0.30 \mu\text{g}/\text{m}^3$ , largely below the  $1.0 \mu\text{g}/\text{m}^3$  annual average standard. However, concentrations of lead in this study were much greater than those in 24 h  $\text{PM}_{2.5}$  or even  $\text{PM}_{10}$  samples measured in Southern California during the fall of 1987 (Chow et al., 1994), while concentrations of copper and bromine were much lower in Beijing. Since leaded fuel has been banned in Beijing since June 1997, the observed lead is assumed to originate from several

sources: re-entrained dust, transport from areas outside of Beijing, vehicle using leaded fuel coming into Beijing, misfueling, non-automotive sources, and trace lead in the fuel supply.

### 3.2.2. Mass balance

Fig. 9 gives the material balance for the average OC, EC, ammonium, nitrate, sulfate, crustal material, trace species, and unexplained mass for the period with both mass and chemical speciation data at the two sites. The material balance was determined according to the method by Christoforou et al. (2000) as follows: (1) multiply OC concentrations by 1.4 to account for unmeasured hydrogen and oxygen in organic materials; (2) sum of the aluminum, silicon, calcium, iron, titanium, manganese and potassium oxides to estimate the crustal material and (3) add the concentrations of all species analyzed by XRF (except for S, Al, Si, Fe, Ti, Mn, Ca, K, Cl, and La) plus  $\text{Mg}^{2+}$  to account for trace species. Assuming potassium to be present as an oxide may not be correct since it was found to be largely soluble and hence is assumed to be associated with biological material.

As noted earlier, organic material is the largest single fraction of the total  $\text{PM}_{2.5}$  mass at both sites. Its contribution was comparable to or larger than that of the major water-soluble ions. Concentrations of organic material and EC were higher at the Tsinghua site than at the Chegongzhuang site, while concentrations of the main secondary particles, i.e., ammonium nitrate and sulfate were relatively spatially homogeneous at the two sites. The crustal material abundance averaged 11–12% in the  $\text{PM}_{2.5}$  mass and their concentrations were close at the two sites. The unexplained portion averaged 20%

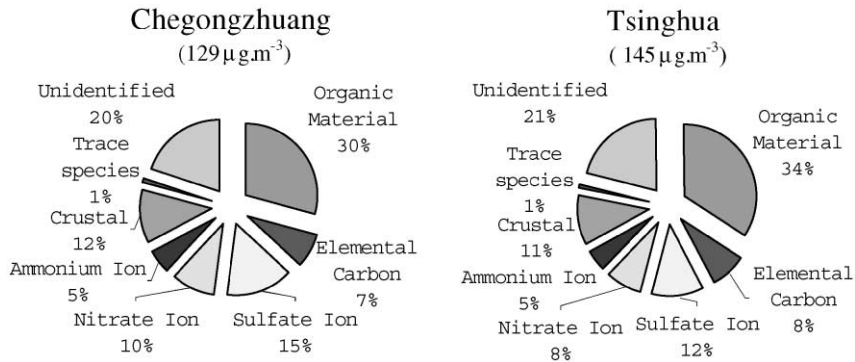


Fig. 9. Average weekly PM<sub>2.5</sub> mass and chemical concentrations between 30 September 1999 and 8 June 2000 at the two Beijing sites.

and 21% of PM<sub>2.5</sub> mass at the Chegongzhuang and Tsinghua sites, respectively. Some of the unexplained mass may be due to systematic weighing errors. Measurements taken with the LFS in another city and analyzed in the same laboratories as in this study had mass balances within 5%. Clearly, more work needs to be done to resolve the source of the unexplained mass.

Source apportionment was carried out using the results of this study. However, it was found that the number of samples was too small for good apportionment by factor analysis, and the chemical mass balance apportionment suffers from a lack of current, local source profiles. Hence, the apportionment will not be presented. Instead, additional monitoring will be conducted and appropriate source profiles will be developed.

### 3.2.3. Other studies

Table 4 compares the Chegongzhuang site results of this study to other PM studies in Beijing or other cities in China. Zhang et al. (1998) collect PM<sub>2.0</sub> samples at five sites in the Beijing area during the autumn and winter of 1992–1993. A total of sixty-two 24 h PM<sub>2.0</sub> samples were collected. Three of the sites were residential while the other two were in industrial areas. Table 4 gives the average observed concentrations of species for the three residential sites for both seasons, since these are most similar to the sites used in this study. The average PM<sub>2.0</sub> mass for the autumn and winter were 133 and 155 µg/m<sup>3</sup>, respectively. Chen et al. (1994) collected PM<sub>2.5</sub> samples in Beijing for 1-week periods for each season in 1989–1990. The results in Table 4 are averages for all the samples. Winchester and Bi (1984) collected 4 h impactor samples in Beijing earlier in 1980. The results in Table 4 are for particles smaller than 2.0 µm. The values are the average over 2 days at several sites. Concentrations for individual impactor stages or the final filter that are reported as being below detection limits were set to zero. Dod et al. (1986) collected 24 h

daily samples in Beijing during the spring, summer and winter of 1983–1984. A low-volume sampler with a PM<sub>12</sub> inlet was utilized. Only those species that are likely to be combustion related are reported in Table 4, since they will be found primarily in the PM<sub>2.5</sub> size range. This includes the total carbonaceous material, which was found to be highly correlated to the sulfur in the winter. Finally, the results of Wei et al. (1999) for PM<sub>2.5</sub> collected in urban areas of Guangzhou, Wuhan, Lanzhou and Chongqing are presented. The values in Table 4 are the averages for the four cities. They represent a total of sixty-six 24 h samples.

Given the lack of historical PM<sub>2.5</sub> data, it is difficult to draw definitive conclusions from the data in Table 4. It is, however, interesting to note that both this and the Chen et al (1994) study reported similar average sulfate concentrations. In addition, the sulfur reported in all studies varied only by a factor of two. TC was also similar in this study and that of Chen et al. (1994), although the OC/EC ratios were very different, presumably due to different analytical techniques. TC was approximately twice as high in the earlier study by Dod et al. (1986), although some of the carbon in that study may have been in the larger particle sizes, and they did not include summer, which was found in this study to have the lowest concentrations. Concentrations of the various elements are also similar in the other Beijing studies and even in the four cities studied by Wei et al. (1999). Zhang and Friedlander (2000) highlighted the earlier reports of high concentrations of fine silicon in Beijing and Lanzhou. Fine silicon in this study and that of Chen et al. (1994) was much lower than that reported by Winchester and Bi (1984). The Winchester and Bi data was collected over a short period of time, and hence may not have been representative of average ambient concentrations. Still, the 2.39 µg/m<sup>3</sup> silicon found in this study is much higher than the 0.27 µg/m<sup>3</sup> report for Los Angeles. The source of that silicon remains uncertain although there clearly is a crustal component since the

Table 4  
Comparison of results to other studies (concentration in  $\mu\text{g}/\text{m}^3$ )

Species	This study (Cheg. site)	Zhang et al. (1998) Autumn	Zhang et al. (1998) Winter	Chen et al. (1994)	Winchester and Bi (1984)	Wei et al. (1999)	Dod et al. (1986)
	PM <sub>2.5</sub>	PM <sub>2.0</sub>	PM <sub>2.0</sub>	PM <sub>2.5</sub>	PM <sub>2.0</sub>	PM <sub>2.5</sub>	PM <sub>12</sub>
SO <sub>4</sub> <sup>2-</sup>	14.47	ND <sup>a</sup>	ND	12.01	ND	ND	ND
OC	21.5	ND	ND	17.41	ND	ND	ND
EC	8.7	ND	ND	16.43	ND	ND	ND
TC	30.2	ND	ND	33.84	ND	ND	63.6
Al	0.8	1.33	2.69	0.763	0.67	ND	ND
Si	2.39	ND	ND	2.71	8.34	ND	ND
Ti	<0.093	0.088	0.19	0.067	0.049	ND	ND
Cr	<0.011	0.0075	0.019	0.1	ND	ND	0.068
P	<0.039	ND	ND	ND	0.1	ND	ND
S	6.57	2.70	6.75	3.987	3.58	6.99	5.72
Cl	2.05	ND	ND	1.433	0.38	1.8	0.95
K	2.83	0.32	1.63	1.335	2.76	ND	3.08
Ca	1.23	2.55	2.85	1.303	1.12	ND	ND
Mn	0.097	0.12	0.12	0.017	ND	ND	ND
Fe	1.14	1.20	1.84	0.794	0.9	ND	ND
Ni	0.015	0.0071	0.012	0.009	0.02	ND	ND
Cu	0.035	0.021	0.039	0.011	0.1	0.041	0.045
Zn	0.48	0.26	0.38	0.313	0.33	0.488	0.535
As	<0.049	ND	ND	0.021	0.018	0.035	0.032
Se	0.009	ND	ND	0.005	ND	0.012	ND
Br	0.017	ND	ND	0.022	0.01	0.052	0.045
Pb	0.304	0.14	0.13	0.21	0.2	0.41	0.31

<sup>a</sup>ND = not determined.

silicon was found to increase dramatically along with other crustal elements during periods impacted by dust storms.

Zhang and Friedlander (2000) constructed a mass balance for the Beijing fine aerosol for the winter period using the limited data available from previous studies. They estimated that the largest components were carbonaceous matter at approximately 50%, ammonium sulfate at approximately 18% and silicon dioxide at approximately 12%. No nitrate data had been reported previously, so nitrate was not included in their mass balance. The winter average in this study shows carbonaceous matter was 31% of the mass when correcting for the associated weight of hydrogen and oxygen, the measured ammonium and sulfate were 18.6% of the mass and silicon dioxide was less than 3% of the mass. If the nitrate is assumed to be present as ammonium nitrate, it would account for approximately 11% of the mass. The greatest difference in the studies is due to the silicon.

#### 4. Summary and conclusions

Mass concentrations, chemical compositions, seasonal variation and site-to-site variations of the PM<sub>2.5</sub> data at

the two Beijing sites have been examined. Little difference was found for the annual average PM<sub>2.5</sub> concentrations between the two sites, which were 115 and 127  $\mu\text{g}/\text{m}^3$  at the Chegongzhuang and Tsinghua sites, respectively. Weekly concentrations ranged from 37 to 357  $\mu\text{g}/\text{m}^3$ .

PM<sub>2.5</sub> mass concentrations exhibited strong weekly variation at both sites, with the maximum difference between two consecutive weeks reaching a factor of 2.5. Obvious seasonal variations of PM<sub>2.5</sub> mass concentrations were observed. PM<sub>2.5</sub> concentrations were highest during the winter, while they tended to be lowest during the summer. PM<sub>2.5</sub> constitutes 64% of PM<sub>10</sub> mass measured by a TEOM.

Much higher coal consumption coupled with meteorology are the likely cause of the high PM<sub>2.5</sub> concentrations in winter. Spring was clearly impacted by dust storms.

Overall, carbonaceous aerosol was the most abundant species and averaged one-third of the PM<sub>2.5</sub> mass, while sulfate, nitrate, and ammonium also were major components. Measured species accounted for 80% of the observed mass. Additional work is needed to improve the mass balance and to obtain the source profiles needed to use this data for source apportionment.

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