Chemical Composition of PM$_{10}$ and PM$_{2.5}$ Collected at Ground Level and 100 Meters during a Strong Winter-Time Pollution Episode in Xi'an, China

Zhenxing Shen$^a$ $^b$, Junji Cao$^b$ $^a$, Suixin Liu$^b$, Chongshu Zhu$^b$, Xin Wang$^a$, Ting Zhang$^b$, Hongmei Xu$^b$ & Tafeng Hu$^b$

$^a$ Department of Environmental Science and Engineering, Xi'an Jiaotong University, Xi'an, People's Republic of China
$^b$ SKLLQG, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, People's Republic of China


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Zhenxing Shen  
Department of Environmental Science and Engineering, Xi’an Jiaotong University, Xi’an, People’s Republic of China; and SKLLQG, Institute of Earth Environment, Chinese Academy of Sciences, Xi’an, People’s Republic of China

Junji Cao  
SKLLQG, Institute of Earth Environment, Chinese Academy of Sciences, Xi’an, People’s Republic of China; and Department of Environmental Science and Engineering, Xi’an Jiaotong University, Xi’an, People’s Republic of China

Suixin Liu and Chongshu Zhu  
SKLLQG, Institute of Earth Environment, Chinese Academy of Sciences, Xi’an, People’s Republic of China

Xin Wang  
Department of Environmental Science and Engineering, Xi’an Jiaotong University, Xi’an, People’s Republic of China

Ting Zhang, Hongmei Xu, and Tafeng Hu  
SKLLQG, Institute of Earth Environment, Chinese Academy of Sciences, Xi’an, People’s Republic of China

ABSTRACT
An intensive sampling of aerosol particles from ground level and 100 m was conducted during a strong pollution episode during the winter in Xi’an, China. Concentrations of water-soluble inorganic ions, carbonaceous compounds, and trace elements were determined to compare the composition of particulate matter (PM) at the two heights. PM mass concentrations were high at both stations: PM$_{10}$ (PM with aerodynamic diameter ≤10 μm) exceeded the China National Air Quality Standard Class II value on three occasions, and PM$_{2.5}$ (PM with aerodynamic diameter ≤2.5 μm) exceeded the daily U.S. National Ambient Air Quality Standard more than 10 times. The PM$_{10}$ organic carbon (OC) and elemental carbon (EC) were slightly lower at the ground than at 100 m, both in terms of concentration and percentage of total mass, but OC and EC in PM$_{2.5}$ exhibited the opposite pattern. Major ionic species, such as sulfate and nitrate, showed vertical variations similar to the carbonaceous aerosols. High sulfate concentrations indicated that coal combustion dominated the PM mass both at the ground and 100 m. Correlations between K$^+$ and OC and EC at 100 m imply a strong influence from suburban biomass burning, whereas coal combustion and motor vehicle exhaust had a greater influence on the ground PM. Stable atmospheric conditions apparently led to the accumulation of PM, especially at 100 m, and these conditions contributed to the similarities in PM at the two elevations. Low coefficient of divergence (CD) values reflect the similarities in the composition of the aerosol between sites, but higher CDs for fine particles compared with coarse ones were consistent with the differences in emission sources between the ground and 100 m.

INTRODUCTION
The chemical composition of the atmospheric aerosol is one of the main factors that determine the particles’ effects on human health and atmospheric visibility.\textsuperscript{1–3} Particulate
matter (PM) is the air pollutant of greatest concern in Xi’an, the largest city in northwestern China (http://www.xianmec.gov.cn/). Several recent studies have investigated the chemical composition and sources of different sized particles in Xi’an, including total suspended particles (TSP) and PM with aerodynamic diameters ≤10 μm (PM10), ≤2.5 μm (PM2.5), and ≤1 μm (PM1). PM2.5 and carbon fractions were studied during the high-pollution seasons of fall and winter in 2004 by Cao et al., and their studies showed carbonaceous aerosol accounted for nearly half of the PM2.5 mass. Motor vehicle exhaust was the major contributor to carbonaceous aerosol in fall, but the influences from coal combustion and biomass burning became more important in winter. Shen et al. reported that sulfate, nitrate, and ammonium were the three major ions both in TSP and PM2.5 from Xi’an, but these ions exhibited different distribution patterns in the four seasons. In addition, the characteristics of ionic species during dust storms and several pollution episodes have been investigated.

These prior studies in Xi’an have all focused on PM collected at ground sites, with the samplers typically deployed 10 to 15 m above ground level (AGL). Unfortunately, little is known about the near-surface variability of aerosol particles in Xi’an, primarily because of the difficulty in making such measurements. Several recent studies on the vertical profiles of aerosol physical and chemical properties in other regions have demonstrated their value in terms of understanding issues involving urban air quality, human health, and urban climate change. For example, Chan et al. investigated the vertical profiles and sources of PM2.5, PM10, and carbonaceous species in Beijing, and they found clear differences between the concentrations and sources for PM and carbon fractions at the ground versus 100, 200, and 325 m. Atmospheric trace gases and particles were measured at heights of 10 and 32 m at the Gustavii Cathedral in Göteborg, Sweden, and that study showed that soil-derived elements and TSP were in greater abundances at the lower level, whereas nitric acid and nitric oxide showed higher concentrations at the upper level. Sulfur dioxide and nitrogen dioxide, as well as many of the elements in the TSP, showed equal concentrations at the two levels.

Xi’an suffered a strong pollution episode from 19 December 2006 to 1 January 2007, and during this event, measurements made by the Shaanxi Meteorological Agency at a station located in northern Xi’an (~6 km away from our sampling site) showed low visibilities, ranging from 0 to 6 km, with a mean value of 1.2 km. During this pollution episode, we conducted an intensive study of PM10 and PM2.5 and associated with ionic species and carbon fractions at a ground site and an elevated site. The aims of the study were to understand vertical variations of PM and chemical composition of aerosol particles, with the expectation that this information would potentially be valuable for planning more effective pollution control strategies.

MATERIALS AND METHODS

Aerosol Sample Collection

Aerosol samples (PM10 and PM2.5) were collected simultaneously at sites that were at elevations of 15 and 100 m AGL (Figure 1). These two sampling sites are both on the campus of Xi’an Jiaotong University, which is in the southeastern part of downtown Xi’an. The ground sampling site was on the roof of a 15-m-high teaching building, whereas the 100-m site was on the flat roof (101 m) of the 107-m-high administration building. The distance between these two sampling sites was ~1 km. To the north of both sites are residential areas and the campus of Xi’an Jiaotong University; to the south are the South Second Ring and Youyi Roads where the traffic is nearly always heavy.

Twenty-four-hour PM10 and PM2.5 (nominally 10:00 a.m. to 10:00 a.m., China Standard Time) daily samples were collected at 15 and 100 m simultaneously from 19 December 2006 to 1 January 2007 using four minivolume samplers (Airmetrics, Springfield, OR). These operated at a flow rate of 5 L min⁻¹, and 47-mm Whatman quartz microfilter fibers (Whatman, Maidstone, UK) were used as collection substrates. Before being used for sampling, the filters were preheated at 800 °C for 3 hr to remove any residual carbon. A total of 52 aerosol samples were collected, and these included 13 pairs of 15-m and 100-m samples. Field blank filters were also collected at both sites by exposing filters in the samplers but not drawing air through them; these were used to account for any artifacts introduced during the sample handling procedure. The exposed filters were placed in clean plastic bags and stored in a refrigerator at ~4 °C until analysis to minimize the evaporation of volatile components.

Aerosol mass loadings were determined gravimetrically using a Sartorius MC5 electronic microbalance (±1 μg sensitivity; Sartorius, Göttingen, Germany). Before weighing, the filters were equilibrated for 24 hr at 20–23 °C in a chamber with a relative humidity between 35% and 45%. Each filter was weighed at least three times before and after sampling following the 24-hr equilibration period. The differences among the three repeated weightings typically were less than 10 μg for blanks and 20 μg for sample filters. The mean net mass for each filter was obtained by subtracting the predeployment weight from the average of the postsampling readings.

It is possible that the PM10 and PM2.5 mass concentrations were influenced by artifacts from sampling with quartz filters rather than Teflon filters, but we note that quartz filters have been used to determine PM mass in prior studies.
Moreover, we used minivolume samplers (flow rate of 5 L min⁻¹) to collect the aerosol samples, and therefore, the artifacts caused by sorption and evaporation of organic substances should be minimal due to the low flow rates. More important, the total aerosol carbon concentrations would appear to be very high compared with any organic artifacts that would have occurred during our study. Accordingly, we simply corrected the data for blank filters to obtain estimates of the organic carbon (OC) contents, as this is the component of the aerosol most likely to be affected by artifacts.

**Water-Soluble Ion Analysis**

The concentrations of four anions (SO₄²⁻, NO₃⁻, Cl⁻, and F⁻) and five cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺) in aqueous extracts of the filters were determined by ion chromatography (IC; Dionex 500, Dionex Corp., Sunnyvale, CA). To extract the water-soluble species from the quartz filters, one-fourth of each filter was put into a separate 20-mL vial containing 10 mL distilled-deionized water (resistivity 18 MΩ)), and then the vials were placed in ultrasonic water bath for 60 min. The samples were shaken twice using a mechanical shaker for 1 hr each time to completely extract the ionic compounds. The extracts were filtered with a 0.45-µm-pore-size microporous membrane, and the filtrates were stored at 4 °C in clean tubes before analysis.

Cation (Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺) concentrations were determined with the use of a CS12A column (Dionex) and 20 mM methanesulfonate as an eluent. Anions (SO₄²⁻, NO₃⁻, Cl⁻, and F⁻) were separated by an AS11-HC column (Dionex), and for this configuration 20 mM KOH was used as the eluent. The method detection limits (MDLs) were 4.6 µg L⁻¹ for Na⁺, 4.0 µg L⁻¹ for NH₄⁺, 10.0 µg L⁻¹ for K⁺, Mg²⁺, and Ca²⁺, 0.5 µg L⁻¹ for F⁻ and Cl⁻, 15 µg L⁻¹ for NO₃⁻, and 20 µg L⁻¹ for SO₄²⁻. Standard reference materials produced by the National Research Center for Certified Reference Materials, China, were analyzed for quality assurance purposes. Blank values were subtracted from sample concentrations.

**Carbonaceous Aerosol Measurement**

A 0.526-cm² punch from the quartz filter was analyzed for elemental carbon (EC) and organic carbon (OC) with the use of a DRI Model 2001 Thermal and Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA). These analyses followed the IMPROVE (Interagency Monitoring of Protected Visual Environments) thermal/optical reflectance protocol, and Data were obtained for four EC fractions (OC1, OC2, OC3, and OC4 in a He atmosphere at 140, 280, 480, and 580 °C, respectively), a pyrolyzed carbon fraction (OPC; determined when reflected laser light attained its original intensity after O₂ was added to the combustion atmosphere), and three EC fractions (EC1, EC2, and EC3 in a 2% O₂/98% He atmosphere at 580, 740, and 840 °C, respectively). The analyzer was calibrated with CH₄ daily. One replicate analysis was performed for each group of 10 samples. Blanks also were analyzed, and the sample concentrations were corrected for those blanks. Additional quality assurance and quality control procedures have been described in detail in Cao et al.²¹

The IMPROVE protocol defines OC as OC1 + OC2 + OC3 + OC4 + OPC and EC as EC1 + EC2 + EC3 – OPC. The mass concentration of organic matter (OM) in atmosphere was estimated by multiplying OC by 1.6.²⁵ The total carbonaceous aerosol (TCA) was calculated as the sum of OM and EC.

**Elemental Fe Analysis and Estimation Crustal Matter Concentrations**

A variety of dust-derived trace elements can be used to estimate the crustal matter concentration, and here Fe was used for this purpose. The aerosol-laden quartz-membrane samples were analyzed to determine Fe concentrations²⁶,²⁷ by energy-dispersive X-ray fluorescence (ED-XRF) spectrometry. The instrument used for these analyses was a Epsilon 5 XRF analyzer (PANalytical, Almelo, The Netherlands) whose X-ray source was a side-window X-ray tube with a gadolinium anode. The analyzer was operated at an accelerating voltage of 25–100 kV and a current of 0.5–24 mA (maximum power: 600 W). The characteristic X-ray radiation was detected with the use of a PAN 32 germanium detector. Comparison tests have been done for PM₂.₅ samples collected simultaneously on quartz and Teflon membranes, and they showed a strong correlation (r = 0.982, P < 0.0001) between the two data sets. That result attests to the accuracy of the Fe concentrations measured on quartz membranes. By repeated (five times) analyses of a single quartz filter sample, the analytical precision for Fe was calculated to be 7.6%. Laboratory quartz blank filter samples were analyzed to evaluate analytical bias, and the detection limit of Fe was calculated to be 24.0 ng m⁻³. Duplicate analyses were performed for every eight samples as a means of guaranteeing the stability and precision of instrument.

Prior studies have shown that Fe accounts for 4% of Asian dust and Chinese loess,²⁸–²⁹ and on this basis, crustal matter concentrations were estimated from the following equation:

\[
C_{\text{crustal matter}} = C_{\text{Fe}}/4\%,
\]

where \(C_{\text{crustal matter}}\) is crustal matter concentration and \(C_{\text{Fe}}\) is the elemental Fe concentration.

**Meteorological Data and Mixed Layer Depths**

Meteorological data, including ambient temperature, relative humidity (RH), wind speed (WS), and visibility, were recorded by the Shaanxi Meteorological Agency. The meteorological station is located in the northern part of Xi’an city, nearly 6 km away from our sampling site. As the mixed-layer depth (MLD) is an important influence on pollution levels, we calculated MLDs using the U.S. National Oceanic and Atmospheric Administration (NOAA; http://www.arl.noaa.gov/ready/hysplit4.html) HYSPLIT4 (Hybrid Single-Particle Lagrangian Integrated Trajectory) model.²⁸–²⁹ For the observational period, MLDs were calculated at 12:00 a.m., 6:00 a.m., 12:00 p.m., and 4:00 p.m. Coordinated Universal Time (UTC) corresponding to Chinese Standard Time (CST) of 8:00 a.m., 2:00 p.m., 8:00 p.m., and 12:00 a.m.

**RESULTS AND DISCUSSION**

**PM Mass Concentrations**

The mass concentrations of PM, OC, EC, and nine water-soluble inorganic ions were determined at the ground and 100-m sites in Xi’an, and the results are summarized in

Shen et al.
Table 1. At the ground site, the mean daily PM$_{10}$ and PM$_{2.5}$ concentrations were 539.8 and 392.1 µg m$^{-3}$, respectively. At 100 m, the PM$_{10}$ mean mass concentration was 538.5 µg m$^{-3}$, which was similar to the ground level, but the PM$_{2.5}$ mass concentration was slightly lower than that at the ground (353.5 µg m$^{-3}$). The average PM$_{10}$ mass at both elevations exceeded the Class II National Air Quality Standard of China (150 µg m$^{-3}$) by more than 3-fold. Moreover, the concentrations of all of the PM$_{2.5}$ samples exceeded the daily U.S. National Ambient Air Quality Standard (35 µg m$^{-3}$), demonstrating the high loadings of both fine and coarse particles in Xi’an.

The PM$_{2.5}$/PM$_{10}$ mass ratio at the ground was 0.71; this is only slightly higher than the ratio of 0.67 at 100 m (Table 2). In fact, the PM$_{2.5}$/PM$_{10}$ concentration ratios for most chemical species were higher at the ground than at 100 m, the exception being crustal matter species. These patterns suggest that particles near the ground, especially anthropogenic species, were produced directly from the emission sources, including motor vehicle exhaust and residential coal combustion. At 100 m, on the other hand, fine particles evidently combined to form larger aggregates. Meteorological data recorded during sampling periods showed high RHs (72% on average) and low WSs (1.2 m sec$^{-1}$) on average), and these conditions likely favored particle aggregation at the higher elevation.

The data for the ground station were generally comparable with the results from prior studies at Xi’an. For example, Cao et al.$^5$ reported that the ground (10 m AGL) mean mass concentrations for PM$_{10}$ and PM$_{2.5}$ were 450.6 and 258.7 µg m$^{-3}$, respectively, in winter at the high-technology zone, demonstrating the high loadings of PM and chemical species. The PM$_{2.5}$/PM$_{10}$ ratio reported by Cao et al.$^5$ was 0.60, which is slightly lower than, but not inconsistent with, the value we observed. Chan et al.$^{16}$ investigated the vertical profiles of PM and carbonaceous species in Beijing in August: there the PM levels were much lower than what was observed at Xi’an either in our study and the prior one by Cao et al.$^5$ Furthermore, the PM$_{2.5}$/PM$_{10}$ ratios reported for Beijing (0.54 at the ground and 0.61 at 100 m) were both lower than the corresponding ratios for Xi’an, indicating coarse particles were relatively more abundant at Beijing than Xian. The differences between these two observations can be explained by meteorology, that is, the prevailing wind during the Beijing study was always above 4 m sec$^{-1}$, whereas at Xi’an the winds were nearly calm and the RH was high. Sasaki and Sakamoto$^{18}$ reported that the PM$_{2.5}$/PM$_{10}$ ratios at Osaka, Japan, averaged 0.83 at ground level and 0.77 at 200 m; both of these values are higher than what we observed in Xi’an.

**Carbonaceous Species**

The mean concentrations of PM$_{10}$ OC and EC at the ground site were 73.7 ± 20.1 and 15.2 ± 5.2 µg m$^{-3}$, respectively; these are nearly the same loadings observed at 100 m (75.0 ± 23.3 and 15.2 ± 4.6 µg m$^{-3}$, respectively). In contrast, the ground PM$_{2.5}$ OC (73.4 ± 24.7 µg m$^{-3}$) and EC (12.0 ± 4.5 µg m$^{-3}$) concentrations were higher than at 100 m (56.7 ± 16.8 µg m$^{-3}$ for OC and 9.5 ± 2.4 µg m$^{-3}$ for EC). Sasaki and Sakamoto$^{18}$ similarly found that the concentrations of carbonaceous species near the ground were higher than those at 200 m, and this was attributed to the abundance of primary particles at the ground. The concentrations of ground PM$_{10}$ carbonaceous species observed in our study were lower than those reported by Cao et al.$^5$ in Xi’an, but they much higher than those observed at Beijing at ground level or 100 m.$^{18}$

### Table 1. Mass concentrations (µg m$^{-3}$) of PM and chemical species.

<table>
<thead>
<tr>
<th>PM Fraction</th>
<th>Mass</th>
<th>OC</th>
<th>EC</th>
<th>Na$^+$</th>
<th>NH$_4$+</th>
<th>K$^+$</th>
<th>Mg$^{2+}$</th>
<th>Ca$^{2+}$</th>
<th>F$^-$</th>
<th>Cl$^-$</th>
<th>NO$_3^-$</th>
<th>SO$_4^{2-}$</th>
<th>Crustal Matter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground PM$_{10}$ (n = 13)</td>
<td>Mean</td>
<td>539.8</td>
<td>73.7</td>
<td>15.2</td>
<td>5.1</td>
<td>29.2</td>
<td>6.9</td>
<td>1.3</td>
<td>10.5</td>
<td>4.1</td>
<td>14.2</td>
<td>60.8</td>
<td>122.3</td>
</tr>
<tr>
<td>SD</td>
<td>133.7</td>
<td>20.1</td>
<td>5.2</td>
<td>1</td>
<td>12.9</td>
<td>2</td>
<td>0.6</td>
<td>4.9</td>
<td>1.2</td>
<td>3.5</td>
<td>27.7</td>
<td>51.2</td>
<td>68.7</td>
</tr>
<tr>
<td>PM$_{2.5}$ (n = 13)</td>
<td>Mean</td>
<td>392.1</td>
<td>73.4</td>
<td>12.0</td>
<td>4.8</td>
<td>28</td>
<td>6.5</td>
<td>0.6</td>
<td>3.0</td>
<td>2.6</td>
<td>12.9</td>
<td>48.9</td>
<td>107.3</td>
</tr>
<tr>
<td>SD</td>
<td>125.7</td>
<td>24.7</td>
<td>4.5</td>
<td>1</td>
<td>13</td>
<td>2.2</td>
<td>0.3</td>
<td>1.6</td>
<td>0.8</td>
<td>3.3</td>
<td>23.7</td>
<td>48.6</td>
<td>14.5</td>
</tr>
<tr>
<td>100 m</td>
<td>PM$_{10}$ (n = 13)</td>
<td>Mean</td>
<td>558.5</td>
<td>75</td>
<td>15.2</td>
<td>5</td>
<td>33.3</td>
<td>7.4</td>
<td>1.3</td>
<td>9.4</td>
<td>4.1</td>
<td>14.4</td>
<td>61.9</td>
</tr>
<tr>
<td>SD</td>
<td>147.3</td>
<td>23.3</td>
<td>4.6</td>
<td>0.9</td>
<td>12.0</td>
<td>2.0</td>
<td>0.6</td>
<td>4.9</td>
<td>1.4</td>
<td>4.3</td>
<td>26.5</td>
<td>46.7</td>
<td>77.9</td>
</tr>
<tr>
<td>PM$_{2.5}$ (n = 13)</td>
<td>Mean</td>
<td>353.5</td>
<td>56.7</td>
<td>9.5</td>
<td>4.3</td>
<td>26.7</td>
<td>6.0</td>
<td>0.6</td>
<td>2.6</td>
<td>2.4</td>
<td>11.2</td>
<td>42.7</td>
<td>97.3</td>
</tr>
<tr>
<td>SD</td>
<td>90.3</td>
<td>15.8</td>
<td>2.4</td>
<td>1.1</td>
<td>7.2</td>
<td>1.6</td>
<td>0.3</td>
<td>1.6</td>
<td>0.8</td>
<td>3.1</td>
<td>21.1</td>
<td>43.3</td>
<td>18.6</td>
</tr>
</tbody>
</table>

Note: SD = standard deviation.

### Table 2. PM$_{2.5}$/PM$_{10}$ ratios of chemical species mass concentrations.

<table>
<thead>
<tr>
<th>Mass</th>
<th>OC</th>
<th>EC</th>
<th>Na$^+$</th>
<th>NH$_4$+</th>
<th>K$^+$</th>
<th>Mg$^{2+}$</th>
<th>Ca$^{2+}$</th>
<th>F$^-$</th>
<th>Cl$^-$</th>
<th>NO$_3^-$</th>
<th>SO$_4^{2-}$</th>
<th>Crustal Matter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground Average</td>
<td>0.71</td>
<td>0.98</td>
<td>0.78</td>
<td>0.97</td>
<td>0.98</td>
<td>0.94</td>
<td>0.44</td>
<td>0.28</td>
<td>0.65</td>
<td>0.92</td>
<td>0.85</td>
<td>0.89</td>
</tr>
<tr>
<td>SD</td>
<td>0.06</td>
<td>0.08</td>
<td>0.08</td>
<td>0.18</td>
<td>0.19</td>
<td>0.08</td>
<td>0.07</td>
<td>0.10</td>
<td>0.16</td>
<td>0.09</td>
<td>0.17</td>
<td>0.09</td>
</tr>
<tr>
<td>100 m Average</td>
<td>0.67</td>
<td>0.77</td>
<td>0.64</td>
<td>0.86</td>
<td>0.84</td>
<td>0.82</td>
<td>0.46</td>
<td>0.31</td>
<td>0.61</td>
<td>0.79</td>
<td>0.74</td>
<td>0.70</td>
</tr>
<tr>
<td>SD</td>
<td>0.10</td>
<td>0.09</td>
<td>0.12</td>
<td>0.17</td>
<td>0.14</td>
<td>0.10</td>
<td>0.19</td>
<td>0.23</td>
<td>0.16</td>
<td>0.09</td>
<td>0.15</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Note: SD = standard deviation.
With reference to PM$_{2.5}$, the OC and EC concentrations at the ground were higher than those at 100 m (Table 1), but they were lower than what was observed at Beijing by Chan et al.$^{18}$ Whereas the ground-level PM$_{2.5}$ OC we observed was lower than that measured by Cao et al.,$^3$ the PM$_{2.5}$ EC was at nearly the same level as in that earlier study. At the ground site, PM$_{2.5}$ OC accounted for 98% of the PM$_{10}$ OC, but the percentage decreased to 77% at 100 m. A similar trend was found for PM$_{2.5}$/PM$_{10}$ EC ratios; these were 0.78 at ground and 0.67 at 100 m. In fact, the vertical patterns of both OC and EC were similar to that of PM mass. A possible explanation for the difference in size fractions between both OC and EC was mentioned above, that is, the aerosol closer to the ground was fresher whereas the PM at 100 m was composed of more aggregates. The mean TCA concentrations at the ground site were 133.1 g m$^{-3}$ for PM$_{10}$ and 121.3 g m$^{-3}$ for PM$_{2.5}$, accounting for 24.7% of PM$_{10}$ and 33.5% of PM$_{2.5}$ mass. At 100 m, the PM$_{10}$ and PM$_{2.5}$ TCA concentrations were 135.2 and 100.2 g m$^{-3}$, equivalent to 25.0% and 28.5%, respectively, of the PM mass.

OC/EC ratios can provide some insight into the origins of carbonaceous aerosols and mechanisms involved in their formation.$^{21,30,31}$ The mean PM$_{10}$ OC/EC ratios were 5.1 at the ground and 5.0 at 100 m; the corresponding PM$_{2.5}$ OC/EC ratios were higher, 6.2 and 6.0. The ground OC/EC ratios were slightly higher than those observed at Xi’an by Cao et al.,$^3$ which were 4.2 for PM$_{10}$ and 5.1 for PM$_{2.5}$. In Beijing, the ground OC/EC ratios for PM$_{10}$ and PM$_{2.5}$ ratios were substantially lower (3.0 and 2.7, respectively) compared with those from our study, and they also were lower at 100 m (2.7 and 2.6, respectively; Chan et al.$^{18}$).

The dissimilar OC/EC ratios at Xi’an and Beijing imply differences in the origins of the carbonaceous aerosol at the two cities. Coal combustion and biomass burning for heating are two of the most important emission sources for carbonaceous aerosol in Xi’an during winter. On the other hand, in Beijing motor vehicle emissions and industrial emissions are the most important source for carbonaceous particles.$^{18}$ Source profiles for carbonaceous aerosols have been measured by Watson et al.$^{32}$ and Cachier et al.$^{33}$ and they reported OC/EC ratios of 1.1 for vehicle exhaust, 2.7 for coal combustion, and 9.0 for biomass burning. Meanwhile, Cao et al.$^3$ reported very high OC/EC ratios for biomass burning (60.3) in Xi’an. Cachier et al.$^{33}$ mentioned that three factors influence the OC/EC ratios; these are emission sources, secondary organic aerosol (SOA) formation, and different removal rates for OC and EC by deposition. Therefore, the emission sources cannot be conclusively identified through the OC/EC ratios alone. Nevertheless, almost all of the OC/EC ratios in the present study exceeded 3.8 for both the PM$_{10}$ and PM$_{2.5}$ samples, and this presumably reflects the contributions from coal combustion and biomass burning superimposed on motor vehicle emissions.

Some subtle but distinct differences between the OC/EC ratios for the ground and 100-m sites were evident. First, the distribution of the OC/EC ratios was broader at the ground than at 100 m. For example, the maximum and minimum ratios of OC/EC at ground were 2.0 for PM$_{2.5}$ and 2.3 for PM$_{10}$, whereas at 100 m they were 1.6 and 1.5. This suggests that a more complex set of sources affected the carbonaceous aerosol at the ground, and these likely included both fresh carbon (from vehicle emissions and coal combustion) as well as aged carbon (secondary carbonaceous aerosol). Second, the OC/EC ratios at ground were higher than those at 100 m, and this is more likely due to aged carbon rather than products from biomass burning. The latter can be evaluated by examining the relationship between EC and water-soluble K$^+$, and this is discussed below.

### Water-Soluble Inorganic Ions

The total PM$_{10}$ ion mass concentration at the ground site was 254.4 μg m$^{-3}$, which was slightly lower than 263.8 μg m$^{-3}$ at 100 m. In contrast, the ground total PM$_{2.5}$ ion mass concentration (214.6 μg m$^{-3}$) was slightly higher than at 100 m (193.8 μg m$^{-3}$). The sum of the measured ions accounted for 46.8% of the PM$_{2.5}$ mass and 54.0% of the PM$_{10}$ at the ground site and 49.0% and 53.7% of the respective PM$_{2.5}$ and PM$_{10}$ mass at 100 m. The high percentages of PM mass accounted for by the water-soluble ions show that they are major components of the PM both at the ground and at 100 m, at least on a mass basis. As shown in Table 1, SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, and Cl$^-$ were the most abundant of the water-soluble inorganic ions, and their concentrations followed the same order at the ground and at 100 m. Sulfate dominated the water-soluble ion mass, and its high concentration is most logically ascribed to the large quantities of coal burned for heating in winter.$^9$ At the ground site, the PM$_{10}$ ion concentrations followed the decreasing order of SO$_4^{2-}$ > NO$_3^-$ > NH$_4^+$ > Cl$^-$ > Ca$^{2+}$ > K$^+$ > Na$^+$ > F$^-$ > Mg$^{2+}$. However, in PM$_{2.5}$ the order of the less abundant ions was somewhat different SO$_4^{2-}$ > NO$_3^-$ > NH$_4^+$ > Cl$^-$ > Na$^+$ > Ca$^{2+}$ > F$^-$ > Mg$^{2+}$ (Table 1).

The PM$_{2.5}$/PM$_{10}$ mass ratios of the ions at the ground site indicated more than 90% of the NH$_4^+$, Cl$^-$, Na$^+$, and K$^+$, 80% of the SO$_4^{2-}$ and NO$_3^-$, and 60% of F$^-$ were in the finer fraction of particles. In contrast, Ca$^{2+}$ and Mg$^{2+}$ were more abundant in the coarse size fraction, presumably because they are mainly from fugitive dust.$^7$ The patterns in the PM$_{2.5}$/PM$_{10}$ ion concentrations at 100 m were similar to those observed at the ground, but the ratios for the ions at the ground were higher than those at 100 m. The two exceptions were the soil-derived species, Mg$^{2+}$ and Ca$^{2+}$, whose PM$_{2.5}$/PM$_{10}$ mass ratios at 100 m were slightly higher than those at the ground. Particle growth by aggregation at the 100-m site is one of the more plausible explanations for the lower PM$_{2.5}$/PM$_{10}$ ratios at that higher site. That is, the high RH and low WS likely enhanced the accumulation of particles at 100 m, whereas the particles closer to the ground were more affected fresh emissions, especially vehicle exhaust and coal burning.

Water-soluble K$^+$ mainly originates from biomass burning,$^{34,35}$ and indeed in the suburbs of Xi’an, wheat straw and maize stalks are widely burned for heating during winter and early spring (from November to April). Here, the relationships between K$^+$ with OC and EC evaluated as a means for further investigating likely sources for the carbonaceous aerosol. As shown in Figure 2, a strong correlation was found between water-soluble K$^+$ and OC both at the ground and at the higher site, indicating important contributions from biomass burning to organic carbon. But the correlation coefficients for the ground site were slightly lower than at 100 m (Figure 2), and this implies that a more complex set of sources influenced the carbonaceous aerosol at the ground.
Moreover, some differences become evident when the correlations for water-soluble K⁺ and EC are compared between the ground and 100 m. That is, water-soluble K⁺ was poorly correlated with EC at the ground, and this suggests stronger contributions from coal combustion and vehicles to the carbonaceous aerosol. In contrast, water-soluble K⁺ was significantly correlated with EC at 100 m (r = 0.69), and this further attests to the important contributions of suburban biomass burning to the carbonaceous aerosol at 100 m.

Comparison of the PM Chemical Composition at the Ground and 100 m

The coefficient of divergence (CD), a self-normalizing parameter, was adopted to compare the spread of the average concentrations of major chemical species at the ground and 100-m sites. The CD is calculated as follows:

$$\text{CD}_{jk} = \sqrt{\frac{1}{p} \sum_{i=1}^{p} \frac{(x_{ij} - x_{ik})^2}{x_{ij} + x_{ik}}}$$

(2)

where \(x_i\) represents the average concentration for a chemical component \(i\) at site \(j\), \(j\) and \(k\) represent two sampling sites, and \(p\) is the number of chemical components. The CDs can be calculated from short-term measurements or long-term averages. In our study, 12 chemical species (OC, EC, Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, SO₄²⁻, NO₃⁻, Cl⁻, F⁻, and Fe) were used to calculate CDs for the ground and 100-m stations. A CD approaching zero supports the null hypothesis, that is, that the two sampling sites were similar for the measured chemical species. If the aerosol composition at the two sampling sites were very different, the CD would approach unity.

The CD value calculated for the ground and 100-m stations was 0.052 for PM₁₀ and 0.118 for PM₂.₅ (Figure 3); these low values indicate that the aerosol composition at the ground and 100 m during the heavy pollution episode were quite similar. The fact that the CD value for PM₂.₅ was roughly doubles that of PM₁₀ shows that the difference in fine particle composition between ground and 100 m was somewhat greater than the difference in coarse particles. These results support the explanation for the differences in the fine particles between ground and 100 m proposed above, that is, the ground PM was more influenced heavily by vehicle exhaust, coal burning, and aged aerosol while biomass burning made a stronger contribution to PM at 100 m.
Effects of Meteorological Conditions on PM and Chemical Species

Low WSs were recorded throughout the sampling period, with a maximum value of 2 m sec\(^{-1}\) (Figure 4). In addition, high RHs were recorded during the study, varying from 45% to 91%, with a mean value of 71.7%. We attribute the high PM levels, both at the ground and 100 m, at least in part, to these conditions. Figure 4 also shows diurnal variations of the mixed layer depths (MLDs) at 12:00 a.m., 6:00 a.m., 12:00 p.m., and 4:00 p.m. Universal Coordinated Time (UTC), which correspond to CST at 8:00 a.m., 2:00 p.m., 8:00 p.m., and 12:00 a.m., respectively. Low MLDs occurred in the evening (at 12:00 a.m. CST and 8:00 p.m. CST) and early morning: the mean MLDs were 95.1 m at

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**Figure 3.** Comparison of average concentrations of chemical species at ground level and 100 m, for (a) PM\(_{10}\) and (b) PM\(_{2.5}\).

**Figure 4.** Variations of wind speed (WS), relative humidity (RH), and mixed layer depth (MLD).
12:00 a.m., 123.2 m at 8:00 p.m., and 79.0 m at 8:00 a.m. CST. In contrast, much higher MLDs were observed at noon (averaged 735.1 m at 2:00 p.m. CST). The shallow MLDs in the evening and morning would tend to favor particle aggregation, whereas the deeper MLDs at noon would lead to the dispersion of air pollutants. In summary, the high PM levels during this serious pollution episode can be attributed to particle accumulation that was facilitated by stable atmospheric conditions.

**Material Balance of PM**

To calculate the mass balance of PM, crustal matter concentrations were estimated from the dust-derived trace element Fe. As shown in Table 1, the PM$_{10}$ crustal matter loading at the ground site was 156.7 μg m$^{-3}$, and that was higher than the 100-m value of 115.0. The higher PM$_{10}$ loading observed at the ground site can be explained by a greater influence of resuspended dust at there. In contrast, the crustal matter loadings for the finer PM$_{2.5}$ size fraction were at the nearly same levels at the two sites.

The relative contributions of measured chemical species to PM mass are shown in Figure 5. For the PM$_{10}$ ground samples, the major components followed the sequence of crustal matter (29.3%), sulfate (22.5%), OM (21.8%), nitrate (11.0%), and ammonium (5.4%). Unidentified materials accounted for 3.8% of PM$_{10}$ mass. In comparison, at 100 m, sulfate (23.8%) was the most abundant component of PM$_{10}$, and it was followed by OM (22.2%), crustal matter (22.0%), nitrate (11.2%), unidentified materials (8.2%), and ammonium (6.2%). Interestingly, the three main secondary aerosol species (sulfate, nitrate, and ammonium) showed no marked vertical variations, either in terms of mass or the percentage of total mass, between the ground and 100-m PM$_{10}$.

The chemical constituents in fine particles were somewhat different compared with coarse particles; that is, the percentage of crustal matter was much lower in PM$_{2.5}$ than PM$_{10}$, whereas the relative abundances of OM, sulfate, and ammonium were higher in the finer particle fraction. In general, the contributions of chemical species to PM$_{2.5}$ mass at the ground and 100 m were similar except for OM and crustal matter. At the ground site, OM contributed to 30.3% to PM$_{2.5}$ mass, and this was followed by sulfate (26.9%), nitrate (12.1%), crustal matter (11.9%), ammonium (7.0%), unidentified materials (4.5%), chloride (3.4%), EC (3.2%), and fluoride (0.7%). At 100 m, however, the percentage of sulfate in PM$_{2.5}$ exceeded that of OM, and the contribution of crustal matter exceeded that of nitrate.
The high sulfate and OM loadings, both in terms of mass concentrations and percentages of total mass, further attest to the importance of coal combustion as a source of air pollution during heating season in Xi’an.

CONCLUSIONS
High PM levels were observed during a serious pollution episode during the winter in Xi’an, China. In general, no dramatic differences of PM and chemical species levels were found between the ground and 100 m; we attribute this to the low wind speeds, high relative humidities, and relatively shallow mixed layers during the study. Water-soluble ions contributed roughly 50% of the PM$_{10}$ and PM$_{2.5}$ mass, and therefore they were major components of the PM both at the ground and at 100 m. The next most abundant aerosol components by mass were carbonaceous materials and crustal matter. High loadings of sulfate and organic matter both in terms of mass concentrations and percentages of total mass demonstrate the impact of the coal burned for heat on air quality. Differences in the partitioning of the chemical species between PM$_{2.5}$ and PM$_{10}$ suggest that the ground PM was more strongly affected by fresh emissions, especially motor vehicle exhaust and coal burning, whereas more particle aggregates were present at 100 m. Good correlations between water-soluble K and Pb suggest that the ground PM was more strongly affected by fresh emissions, especially motor vehicle exhaust and coal burning, whereas more particle aggregates were present at 100 m. Good correlations between water-soluble K and Pb suggest that the ground PM was more strongly affected by fresh emissions, especially motor vehicle exhaust and coal burning.

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**About the Authors**

Zhenxing Shen (Associate Professor) and Xin Wang (postgraduate student) are in the Department of Environmental Science and Engineering, Xi’an Jiaotong University, Xi’an, China. Junji Cao (professor), Chongshu Zhu (assistant professor), Suixin Liu (assistant professor), Ting Zhang (assistant professor), Hongmei Xu (postgraduate student), and Tafeng Hu (postdoctoral scholar) work for the institute of Earth Environment, Chinese Academy of Sciences, Xi’an, China. Please address correspondence to: Zhenxing Shen, Department of Environmental Science and Engineering, Xi’an Jiaotong University, Xi’an 710049, China; e-mail: zxshen@mail.xjtu.edu.cn.