Chemical Characteristics of PM$_{2.5}$ during a 2016 Winter Haze Episode in Shijiazhuang, China

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ABSTRACT

To better understand the chemical characteristics and the potential source regions of PM$_{2.5}$ measured from 18 January until 22 January 2016 in Shijiazhuang, China, PM$_{2.5}$ was measured continuously and integrated daily sampling using mid-volume samplers was conducted at the three sites. The mean concentration of PM$_{2.5}$ at the three sites reached 113, 131 and 119 µg m$^{-3}$ during the sampling period, the higher concentrations occurred at early morning and noon, similar variation trends were found in the three sites. The concentrations of OC were higher than EC at three sampling sites and the OC/EC ratios ranged from 9.09 to 12.4 with a daily mean value of 10.8 during a haze pollution episode (HPE), which suggested that carbonaceous compositions might be from same source. The total concentration of water soluble inorganic ions (WSII) at the sites ranged from 72.2 to 100.0 µg m$^{-3}$ with a mean of 84.3 µg m$^{-3}$. The dominant species were NO$_3^-$, SO$_4^{2-}$, NH$_4^+$, Cl$^-$, accounting for 88.4% of the mean PM$_{2.5}$ WSII mass. The most abundant measured element was Na with average mass concentrations of 41.5, 37.0, and 38.1 µg m$^{-3}$ during the HPE. Relative humidity during HPE was higher than during clean days with average values of 70.1% and 60.2%, suggesting that high relative humidity and low wind speed favored formation of secondary inorganic ions and accelerated hygroscopic growth. The Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) and a potential source contribution function (PSCF) analysis were used to assess the data. Back-trajectories for the three sites identified similar transport pathways. PSCF analysis showed a significant regional impact on PM$_{2.5}$ at Shijiazhuang during the polluted period. The potential source areas for PM$_{2.5}$ in Shijiazhuang were the Beijing-Tianjin region and Shandong Province. The results of the present study show the need for the development of PM$_{2.5}$ control measurements on a regional scale.

Keywords: PM$_{2.5}$; Chemical composition; Meteorological factors; Backward trajectory; Potential source contribution function (PSCF).

INTRODUCTION

Since January 2013, China has been suffering severe and long-term haze pollution events. PM$_{2.5}$ (particle matter with an aerodynamic diameter of less than or equal to 2.5 µm) has been found to be the most important constituent (Deng et al., 2016; Gautam et al., 2016; Qiao et al., 2016). According to the “2014 report on the state of the environment in China” (MEP, 2014), 11.2% of the 161 cities in China met the annual average concentration of PM$_{2.5}$ Grade II standard of 35 µg m$^{-3}$ and 24-hour average of 75.0 µg m$^{-3}$. Many studies show that both anthropogenic sources emissions and meteorological conditions play significant roles in formation and transmission of haze pollution (Mansha et al., 2012; Chen et al., 2014; Yang and Christakos, 2015; Yao et al., 2016). In addition, haze pollution is usually accompanied by high mass concentrations and has strong impacts on human health, visibility, ecosystems and climate change. Toxic chemical components and pathogenic organisms on particles can cause further harm to the human health with acute and chronic effects (Iii et al., 2002; Künzli and Hodis, 2005; Johanna et al., 2012).

Shijiazhuang, capital of Hebei Province, is ranked as the 2nd most polluted city in China with a highest hourly average concentration of PM$_{2.5}$ of more than 750 µg m$^{-3}$ and extraordinarily persistent haze. According to a related study (Wang et al., 2015a), the regional source contributions to PM$_{2.5}$ in Shijiazhuang were 27.9%, while the major local contributions were industrial, domestic and agricultural
sources, which contributed for 39.8%, 15.8% and 10.6%, respectively. A series of air pollution control measures has been taken by Shijiazhuang government. More desulfurization systems and desulfurization facilities have been installed in the iron, steel, cement, and coke industries. Old boilers and chimneys have been demolished. Removal of 54,600 "yellow label cars" has been effected at the end of 2015. By the end of 2017, coal-fired boiler with sizes below 10 tons of coal burned per hour would be phased out. Complete oil and gas vapor recovery systems have been installed at the end of 2013 on 13 oil storage, 769 petrol stations and 234 oil tank trucks. The ratio of the urban centralized heating reached more than 80% (http://www.china-ep.com/law/201402/25/12.html). However, the ambient concentrations of PM still significantly exceed the air quality standard and particulate air pollution remains very serious.

In recent years, many studies have been conducted to characterize the chemical properties of PM$_{2.5}$ in megacities (Heo et al., 2008; Pindado et al., 2009; Elbayoumi et al., 2013; Pey et al., 2013; Masiol et al., 2014), but only limited data have been reported for Shijiazhuang pollution characteristics. It is useful to investigate its spatial distribution, influencing factors, and potential sources of haze pollution. Given that haze pollution events occur frequently in the winter, continuous and speciation PM sampling was conducted at three sites of Shijiazhuang City in January 2016. The main objectives of this study are to: (1) understand the PM$_{2.5}$ concentrations in Shijiazhuang; (2) quantify the spatial trends of PM$_{2.5}$ and its major chemical constituents in Shijiazhuang; (3) estimate the influence of meteorological factors on PM$_{2.5}$ pollution and (4) identify the transport pathway and potential sources of PM$_{2.5}$ by using backward air parcel trajectories and PSCF analysis.

**EXPERIMENTAL METHODS**

**Sampling Sites**

The sampling sites were located at three monitoring sites in Shijiazhuang, as shown in Fig. 1. Site 1 (38.142°N, 114.618°E) is located in Dongchaili village in the northern part of the city, which is far from industrial plants and represents a suburban area. Site 3 (37.892°N, 114.511°E) is located in Yuanshi county in the southern part of the city, represents an urban area. Site 2 (37.892°N, 114.522°E) is located in Hebei Normal University at the center of the city and represent an urban area. Site 3 (37.892°N, 114.511°E) located in Yuanshi county in the southern part of the city, represents a suburban area. All the three sampling sites are set on the rooftops of buildings that are approximately 9–15 m above ground level.

**Ambient Sampling**

The national air quality forecast system of Ministry of Environmental Protection, China, forecast a haze pollution event from 19 January until 21 January 2016. The sampling campaign was conducted from 18 January until 22 January 2016 during which PM$_{2.5}$ samples were collected using two mid-volume samplers (TH-150C, Wuhan Tianhong Ltd., China) for 23 hours at a constant flow rate of 100 L min$^{-1}$. Each site had two samplers started at the same time. Quartz fiber filters with 90 mm diameters were used for the elemental carbon (EC), organic carbon (OC) and water soluble ions analyses. The 90 mm diameter Teflon filters were used for the elemental analysis.

All filters were equilibrated (41% relative humidity, 25°C) for 48 h before and after sampling, and weighed with an electronic balance (0.01 mg precision, Sartorius BT 25S, Germany). Before sampling, the quartz fiber filters were heated at 450°C for 6h to reduce the OC blank values. After sampling, the filters were immediately placed in pre-baked aluminum foil and then stored frozen at –18°C until analyzed.

In addition, PM$_{2.5}$ and PM$_{10}$ mass concentrations were measured using a tapered element oscillation microbalance instruments (TEOM, TEOM Series 1400a, Thermo Fisher Scientific Environmental Instrument Co., Ltd.) operated at the three sampling sites. Details of the TEOM operation can be found in Green and Fuller (2006).

**Chemical Analysis**

The chemical constituents of PM$_{2.5}$ included carbonaceous components, water soluble ions and inorganic elements. The quartz-fiber was cut into pieces for various measurements in each analysis. OC and EC were measured by a Desert Research Institute (DRI) Model 2001 carbon analyzer (Atmoslytic Inc., USA) with IMPROVE-A protocol (Zong et al., 2015). The analyzer was calibrated before and after each sample analysis.

Water soluble ions including three anions (Cl$^-$, SO$_4^{2-}$, NO$_3^-$) and five cations (NH$_4^+$, Ca$^{2+}$, Na$^+$, Mg$^{2+}$, K$^+$) were analyzed by ion chromatography (ICS-90, Dionex, USA) following the method of Yang et al. (2015). Before analysis, the filters were ultrasonically extracted three times, for 15 min each time, with 10 ml deionized water (Milli-Q, 18.2 MΩ cm). The detection limits for eight ions were calculated as three times the standard deviations of replicate blank samples. Quality assurance was routinely conducted using standard reference materials (125052, Merck Co., USA). Blank values were subtracted from the corresponding sample data after analysis.

The elements (Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Ba and Pb) were analyzed by using inductively coupled plasma - mass spectrometry (ICP-MS, Agilent 7500a, Agilent, USA). Before analyzed by ICP-MS, punches (20 mm diameter) from the filters were digested in Teflon vessels with 6 ml concentrated HNO$_3$, 2 ml HCl, and 0.2 mL HF by using a microwave digestion system (MARS 5, CEM Corporation, Matthews, NC, USA) and then diluted with de-ionized water to 50 mL (Li et al., 2013). The resolution of the ICP-MS ranged from 0.3 to 3.0 amu, with a detection limit below 0.01 ng m$^{-3}$. Quality control was performed by making parallel analyses of the reference material GB/T 14506.30-2010. Field blanks accompanied the samples to the sampling sites, and the laboratory control blanks were measured and subtracted from the loaded filters in the above mentioned analysis. The results of each sample for elements were subtracted from the filter blanks results. The average recoveries of the five surrogates ranged from 70% to 120%. The elemental data reported in this report were not corrected by the recoveries.
Fig. 1. Location of the sampling site.
**Meteorological Parameters**

During the sampling period, meteorological parameters, such as temperature (T), relative humidity (RH) and wind speed (WS), were obtained from Shijiazhuang Environmental Monitoring Center Station.

**Air Parcel Back Trajectories and the Potential Source Contribution Function**

In order to better understand the transport of airborne particles from distant sources and the pathway of the air mass, backward trajectories simulations were conducted using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) 4.0 Model developed by NOAA/ARL (Stein et al., 2015) (with meteorological data from the Global Data Assimilation System, GDAS (http://www.rl.noaa.gov/ss/transport/archives.html)). Trajectories extending 3 days (72 h) into the past were estimated for every hour on each day. The trajectories from each site were calculated starting at 500 m above ground level (AGL).

The calculated backward trajectories were applied in performing a PSCF analysis of the PM$_{2.5}$ at the three sites in Shijiazhuang, which had used to identify potential source-areas in other studies (Zeng and Hopke, 1989; Hafner and Hites, 2003; Hoh and Hites, 2004; Liu et al., 2015). In this study, the PM$_2.5$ criterion value was set to 75 µg m$^{-3}$, the 24-hour NAAQS concentration limit. All hourly endpoints in the grid cell. To reduce the effect of small endpoints in the grid cell. To reduce the effect of small

$$PSCF_{ij} = \frac{m_p}{n_p}$$

where PSCF$_{ij}$ is the conditional probability value grid cell $ij$, $m_p$ is the number of endpoints for the same cell corresponding to the fine particles concentrations higher than a setting criterion value and $n_p$ is the total number of endpoints in the grid cell. To reduce the effect of small values of $n_p$, the PSCF values were multiplied by a weighting function (Zeng and Hopke, 1989):

$$w = \begin{cases} 1.0 & 36 < n_p \\ 0.7 & 12 < n_p \leq 36 \\ 0.4 & 8 < n_p \leq 12 \\ 0.2 & 0 < n_p \leq 8 \end{cases}$$

**RESULTS AND DISCUSSION**

**The Temporal and Spatial Variations of PM$_{2.5}$ and PM$_{10}$**

The temporal and spatial variations of PM$_{2.5}$ and PM$_{10}$ hourly mass concentrations from 18 January till 22 January 2016 at three sites are shown in Fig. 2. The average PM$_{2.5}$ values for the month of January as measured at 7 sites around Shijiazhuang are shown in Supplementary Fig. S1. It can be seen that the event between January 19 and 21 is one of several occurring during this month. The hourly values of PM$_{2.5}$ and PM$_{10}$ at site 1 ranged from 4 to 300 µg m$^{-3}$ with an average of 113 µg m$^{-3}$ and from 36 to 411 µg m$^{-3}$ with an average of 172 µg m$^{-3}$, respectively. The haze pollution episode (HPE), defined in this study as daily average concentrations of PM$_{2.5}$ higher than 75 µg m$^{-3}$ occurred from January 19 to January 21. The highest PM$_{2.5}$ and PM$_{10}$ concentrations reached 348 µg m$^{-3}$ and 444 µg m$^{-3}$ at midnight on January 19 at site 2.

Fig. 2 shows that generally the higher concentrations occurred in early morning and at noon. Similar variations were observed at all three sites. The variation and the enhancement of PM$_{2.5}$ can be influenced by local sources, long-range transport, and meteorological condition. A detailed discussion on the meteorological conditions is presented in Section 3.3.

In addition, average ratios of PM$_{2.5}$/PM$_{10}$ were calculated to examine differences in particle size fractions during the HPE and on clear days (CD). The PM$_{2.5}$/PM$_{10}$ ratios during the HPE at all three sites were 0.66, 0.75, and 0.71, respectively, while the values during CD were 0.42, 0.67, and 0.57, respectively. Thus, during the HPE or on CD, PM pollution was dominated by fine particles, except at site 1 during CD. The site 2 values were higher than the other two sites during both HEP and CD suggesting the strong influence of local sources in the city center such as traffic.

**Chemical Species**

**Carbonaceous Components**

Airborne carbonaceous materials, including elemental carbon (EC) and organic carbon (OC), are the major components to the PM$_{2.5}$ burden in the atmosphere of urban and heavily industrialized locations (Gray and Cass, 1998). The overall average values of the concentrations of OC and EC are shown in Table 1. Since EC is emitted from combustion sources and the chemical transformations of elemental carbon is slow, it is a good tracer of primary OC that is typically co-emitted. OC can be emitted from primary emission sources or generated by chemical reactions in the atmosphere.

The concentrations of OC were higher than EC at three sampling sites. The average concentrations of EC (11.3 µg m$^{-3}$) at site 3 were higher than the other two sites. Site 3 is near a freight hub terminal with substantial heavy truck traffic and residential coal combustion was also an important PM source. The high OC concentration (112 µg m$^{-3}$) at site 1 might be due to the residential heating with coal (Zikova et al., 2016). However relatively low concentrations of OC and EC were observed at site 2 suggesting that PM pollution present the rural areas largely from space heating and cooking encircles sites 1 and 3 during the HPE. The concentrations of OC and EC during CD were 19.2 and 3.78 µg m$^{-3}$, respectively. The concentrations of OC and EC reported in various cities are given in Table 2. It is found that the mean concentrations of OC and EC in PM$_{2.5}$ in Shijiazhuang were higher than any other cities (Park et al., 2002; Viana et al., 2007; Feng et al., 2015; Khan et al., 2015; Zhang et al., 2016). The concentrations of PM$_{2.5}$ during the sampling period were also higher than reported for the other cities.
Fig. 2. Temporal and spatial of PM$_{2.5}$ and PM$_{10}$ hourly mass concentration at the three sites during the sampling period.

The ratio of OC/EC could be used to gain some insights regarding the emission and transformation characteristics of carbonaceous aerosol (Cao et al., 2004). According to previous studies (Chow et al., 1996; Watson et al., 2001; Zhang et al., 2008), an OC/EC ratio of 4 was obtained from fossil fuel combustion and 1.1 for vehicle emissions, while biomass burning and residential coal combustion had values of 10.0 to 16.3 and 8.5 to 13.0, respectively. In our study, the OC/EC ratios ranged from 9.1 to 12.4 with a daily mean value of 10.8 during the HPE (Table 1). The small range and high average OC/EC value suggested that the carbonaceous components might largely be from same source and the ratios of OC/EC were consistent with residential coal combustion.

To investigate the contribution of secondary organic carbon (SOC) to OC, the EC-tracer method proposed by Turpin and Huntzicker (1995) was used to estimate SOC
above, this “SOC” may represent primary emissions from poor combustion of coal or biomass. Recently, Zikova \textit{et al.} (2016) suggested substantial amounts of primary sulfate associated with space heating.

Improved stoves (Yan, 2016) to reduce the emissions there are currently plans to provide better quality coal and OC arising from poor combustion of coal in Beijing.

$\text{OC sec} = \text{OC tot} - \text{EC} \times \text{EC/EC min}$

where $\text{OC sec}$ is the concentration of SOC; $\text{OC tot}$ is the concentration of total OC; $\text{EC/EC min}$ is the lowest observed OC/EC ratio during the study period, and EC is the measured EC concentration. The average SOC concentrations at the three sites were 71.3, 40.4, and 49.3 $\mu$g m$^{-3}$ during the HPE accounting for 63.4%, 56.1% and 46.1% of OC, respectively. Higher RH may accelerate multiphase chemical reactions resulting in increasing the SOC concentration during haze days (Zhang \textit{et al.}, 2015). However, as noted above, this “SOC” may represent primary emissions from poor combustion of coal or biomass. Recently, Zikova \textit{et al.} (2016) suggested substantial amounts of primary sulfate and OC arising from poor combustion of coal in Beijing. There are currently plans to provide better quality coal and improved stoves (Yan, 2016) to reduce the emissions associated with space heating.

Water Soluble Ions

Water soluble inorganic ions (WSII) such as Cl$^-$, SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, Ca$^{2+}$, Na$^+$, Mg$^{2+}$ and K$^+$ are important constituents of atmospheric fine particles (Table 3). The total concentration of WSII at three sites ranged from 72.2 to 100.0 $\mu$g m$^{-3}$ with a mean of 84.3 $\mu$g m$^{-3}$ (Table 3). Compared to other studies, the concentrations of WSII in PM$_{2.5}$ during the HPE were significantly higher (Xu \textit{et al.}, 2014; Yang \textit{et al.}, 2015; Lai \textit{et al.}, 2016). NO$_3^-$ was 27.6% of WSII, followed by SO$_4^{2-}$ (26.0%), NH$_4^+$ (18.6%), Cl$^-$ (12.4%), Ca$^{2+}$ (7.4%), Na$^+$ (4.2%), K$^+$ (2.6%), and Mg$^{2+}$ (1.2%). The dominant species were NO$_3^-$, SO$_4^{2-}$, NH$_4^+$, Cl$^-$, accounting for 84.7% of the total WSII mass. These ionic species exhibited similar trends with studies in Beijing (Zikova \textit{et al.}, 2016; Zhang \textit{et al.}, 2016). The concentrations of WSII in PM$_{2.5}$ during CD ranged from 0.463 to 5.65 $\mu$g m$^{-3}$, and the dominant species were SO$_4^{2-}$, Ca$^{2+}$, NH$_4^+$, and NO$_3^-$, accounting for 81.6% of the total WSII mass. The average concentration of NO$_3^-$, SO$_4^{2-}$, NH$_4^+$ and Cl$^-$ at three sites were 27.9, 24.0, 16.8, and 10.5 $\mu$g m$^{-3}$, 24.8, 22.5, 15.1, and 9.7 $\mu$g m$^{-3}$, 22.7, 21.4 15.3, and 10.2 $\mu$g m$^{-3}$ in PM$_{2.5}$ during HPE, respectively. These were 6.5, 3.9, 4.0, and 7.7 times higher, respectively, than those values measured during CD. Han \textit{et al.} (2015) reported that the concentrations of NO$_3^-$, SO$_4^{2-}$, and NH$_4^+$ on haze days were 3.4, 4.3, and 5.2 times higher than those in normal days in Beijing in 2006. These results suggested that WSII plays an important role in forming haze. High chloride is an indicator of coal combustion (Zikova \textit{et al.}, 2016). Yu \textit{et al.} (2013) suggested very high Cl content in coals used in the Beijing area. The enhancements of NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$ during haze days were probably due to fast conversion of their precursors via multiphase reactions at the high relative humidity values (Sun \textit{et al.}, 2006; Ram and Sarin, 2011) as well as the emission of some primary sulfate from the residential coal combustion (Huang \textit{et al.}, 2014; Zikova \textit{et al.}, 2016).

Inorganic Elements

Eighteen elements in PM$_{2.5}$ at three sites were investigated in this study (Table 4). The most abundant element was Na with an average mass concentration of 41.5, 37.0, and 38.1 $\mu$g m$^{-3}$ during CD. The total concentration of the crustal elements

<table>
<thead>
<tr>
<th>City</th>
<th>season</th>
<th>OC (µg m$^{-3}$)</th>
<th>EC (µg m$^{-3}$)</th>
<th>OC/EC</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shijiazhuang</td>
<td>Winter</td>
<td>97.1</td>
<td>8.52</td>
<td>11.5</td>
<td>this study</td>
</tr>
<tr>
<td>Lin’an</td>
<td>Winter</td>
<td>12.2</td>
<td>1.82</td>
<td>6.68</td>
<td></td>
</tr>
<tr>
<td>Beijing</td>
<td>Winter</td>
<td>20.4</td>
<td>4.90</td>
<td>4.20</td>
<td>Zhang \textit{et al.}, 2016</td>
</tr>
<tr>
<td>Belluno</td>
<td>Winter</td>
<td>4.90</td>
<td>1.30</td>
<td>4.40</td>
<td>Khan \textit{et al.}, 2015</td>
</tr>
<tr>
<td>Seoul</td>
<td>Winter</td>
<td>15.2</td>
<td>4.90</td>
<td>2.40</td>
<td>Park \textit{et al.}, 2002</td>
</tr>
<tr>
<td>Barcelona</td>
<td>Winter</td>
<td>5.25</td>
<td>2.05</td>
<td>3.10</td>
<td>Viana \textit{et al.}, 2007</td>
</tr>
</tbody>
</table>

Table 1. The average concentrations of the carbonaceous components of PM$_{2.5}$ samples at the three sites during HPE and CD collected in Shijiazhuang.

<table>
<thead>
<tr>
<th>Species</th>
<th>Haze Pollution Episode</th>
<th>Clean Day</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Site 1</td>
<td>Site 2</td>
</tr>
<tr>
<td>OC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OC/EC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOC</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Organic and elemental carbon concentrations in various cities.
Table 3. The average concentrations of the water soluble ions of PM$_{2.5}$ samples at the three sites during HPE and CD collected in Shijiazhuang.

<table>
<thead>
<tr>
<th>Species</th>
<th>Haze Pollution Episode</th>
<th>Clean Day</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Site 1</td>
<td>Site 2</td>
</tr>
<tr>
<td></td>
<td>Min.</td>
<td>Max.</td>
</tr>
<tr>
<td>µg m$^{-3}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>5.41</td>
<td>15.8</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>17.6</td>
<td>30.4</td>
</tr>
<tr>
<td>NO$_3^-$</td>
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<td>30.6</td>
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<tr>
<td>NH$_4^+$</td>
<td>14.5</td>
<td>18.8</td>
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<td>Ca$^{2+}$</td>
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<tr>
<td>Mg$^{2+}$</td>
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<td>0.82</td>
</tr>
<tr>
<td>K$^+$</td>
<td>1.69</td>
<td>2.95</td>
</tr>
<tr>
<td>WSH</td>
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<td>100</td>
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Table 4. The average concentrations of the inorganic elements of PM$_{2.5}$ samples at the three sites during HPE and CD collected in Shijiazhuang.

<table>
<thead>
<tr>
<th>Species</th>
<th>Haze Pollution Episode</th>
<th>Clean Day</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Site 1</td>
<td>Site 2</td>
</tr>
<tr>
<td>µg m$^{-3}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>31.4</td>
<td>58.9</td>
</tr>
<tr>
<td>Mg</td>
<td>7.35</td>
<td>14.3</td>
</tr>
<tr>
<td>Al</td>
<td>6.60</td>
<td>13.0</td>
</tr>
<tr>
<td>K</td>
<td>2.61</td>
<td>5.28</td>
</tr>
<tr>
<td>Ca</td>
<td>11.0</td>
<td>22.2</td>
</tr>
<tr>
<td>Fe</td>
<td>1.71</td>
<td>3.92</td>
</tr>
<tr>
<td>ng m$^{-3}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>168</td>
<td>493</td>
</tr>
<tr>
<td>V</td>
<td>4.94</td>
<td>9.67</td>
</tr>
<tr>
<td>Cr</td>
<td>59.2</td>
<td>141</td>
</tr>
<tr>
<td>Mn</td>
<td>61.4</td>
<td>134</td>
</tr>
<tr>
<td>Co</td>
<td>1.54</td>
<td>3.39</td>
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<td>Ni</td>
<td>19.7</td>
<td>34.8</td>
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<tr>
<td>Cu</td>
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<td>Zn</td>
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<tr>
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<td>85.1</td>
<td>324</td>
</tr>
<tr>
<td>Pb</td>
<td>119</td>
<td>367</td>
</tr>
</tbody>
</table>

(Na, Ca, Mg, Al, K and Fe) varied from 70.9 to 83.9 µg m$^{-3}$ (mean value: 77.5 µg m$^{-3}$) at the three sites during the HPE, accounting for 98.2% of the measured elements. Likely sources include traffic with its associated road dust and coal combustion (Zikova et al., 2016). The difference of the elemental concentration was relatively small. Thus, the haze pollution must be mainly secondary pollution. The concentrations at site 1 and site 2 were higher than the values of site 3, agreed with the above mentioned results from carbonaceous components.

Additionally, eleven trace elements (V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Ba and Pb) accounted for a small part (1.8%, 1.6%, and 1.9%) of the total elements. The most abundant trace element was Zn with an average mass concentration of 420, 343 and 446 ng m$^{-3}$, respectively. The sources of Zn, As, and Pb are generally anthropogenic. These trace elements tend to have negative effect on human health (Magari et al., 2002; Shi et al., 2010), therefore more measurements would be taken to reduce the anthropogenic sources.

Impact of Meteorological Parameters on Haze Formation

Meteorological parameters during HPE and CD are showed in Fig. 3. The variation trends of wind speed, relative humidity and visibility across the three sites were almost identical. The temperature showed no significant differences between HPE and CD. However, wind speeds were lower during HPE compared to the CD period. The average wind speed was 2.1 m s$^{-1}$ and 3.7 m s$^{-1}$, respectively. A high relative humidity was found to favor the formation of
secondary inorganic ions and accelerate hygroscopic growth (Gasparini et al., 2006; Y. Liu et al., 2008). In this study, relative humidity during HPE was higher than the data during CD, and the average relative humidity was 70.1% and 60.3%, respectively. The results were similar with other cities (Hua et al., 2015). In general, the main meteorological differences between HPE and CD were the relative humidity and wind speed.

**Influence of Air Masses Transport and Potential Source Contribution Function Analysis**

Seventy-two-hour back trajectories were calculated using the HYSPLIT model to get insight into the origin and transport pathway of the air masses arriving at three sampling sites. The optimum number of clusters was established by analyzing the change in the total spatial variance. As illustrated in Fig. 4, the back-trajectories of site 1 were classified into 5 clusters, and clusters 1, 2, 3, 4 and 5 comprise 37.5%, 13.3%, 30.0%, 10.0% and 9.17% of the back-trajectories, respectively. Cluster 1 included back-trajectories from Beijing that also travelled through metropolitan Tianjin. Thus, the air masses backward trajectories were short, indicating air masses move slowly and pollutants were able to accumulate. Many studies indicated that the Beijing–Tianjin region and Shandong Province are a severely polluted region (Yang et al., 2011; Gu et al., 2014; Wang et al., 2015b; Zikova et al., 2016). Both cluster 2 and cluster 3 showed air masses moving from the northern Russia. They also mixed with the emissions from Mongolia. These trajectories reflected the features of large-scale, long-distance air transport, suggesting that the air masses move fast and help to dilute the PM$_{2.5}$ concentrations. Cluster 4 consisted of the backward trajectories originating from the northwestern Mongolia, passing over Inner Mongolia and Shanxi Province prior to arriving at site 1. Cluster 5 represented only 9.17% of the total and began in northwestern Xinjiang Uygur Autonomous Region, travelling through Mongolia, Inner Mongolia and Shanxi Province. By matching the hourly PM$_{2.5}$ concentrations to the trajectory, and define the concentration of PM$_{2.5}$ greater than 75 µg m$^{-3}$ as the criterion, all 45 trajectories of cluster 1 exceeded the criterion with a mean value of 173 µg m$^{-3}$. PSCF also identified the potential source areas for PM$_{2.5}$ of site 1 were Beijing, Hebei and Jinan, which were generally consistent with the backward trajectory analysis results (Fig. 5).

The back-trajectories to site 2 were classified into 6 clusters that account for 40.0%, 2.50%, 14.2%, 26.7%, 9.2% and 7.5% of the back-trajectories, respectively. Cluster 1 showed similar air masses back-trajectories with site 1, and reflected small-scale, short-distance transport. Both cluster 2 and 4 showed air masses moving from the northeastern Russia. These trajectories were long and had a positive effect on the PM$_{2.5}$ concentrations. Cluster 3 and 5 originated from southern Russia, passing over Mongolia, Inner Mongolia and Shanxi Province. Cluster 6 began in the northern of Xinjiang Uygur Autonomous Region, traveling Inner Mongolia and Shanxi Province. These trajectories had little impact on air quality at site 2. PSCF analysis (Fig. 5) also indicated that Beijing, Tianjin, Hebei and northwest of Shandong were generally the main source-regions, further supporting the backward trajectory results.

The back-trajectories at site 3 were classified into 3 clusters accounting for 41.7%, 31.7% and 26.7% of the back-trajectories, respectively. The air masses backward trajectories were quite similar to those for site 1, where the highest PM$_{2.5}$ values were related to trajectories from Beijing, Tianjin, Hebei and northwest Shandong. Similar results were found by PSCF analysis (Fig. 5). Overall, Shijiazhuang
Fig. 4. Results of the back-trajectory cluster analysis for the three sites.
Fig. 5. PSCF plot showing likely PM$_{2.5}$ source regions. Different colors represent the various PSCF values.
was adversely affected mainly by the air masses originating from Beijing-Tianjin (cluster 1), which was also the main potential source-area affecting the atmospheric quality in Shijiazhuang identified by the PSCF analyses.

**CONCLUSION**

New information regarding ambient PM$_{2.5}$ in Shijiazhuang in winter has been developed. The mean concentration of PM$_{2.5}$ in three sites reached 113, 131 and 119 µg m$^{-3}$ during the sampling period. The higher concentrations occurred in the early morning and at noon. Similar temporal trends were found at all three sites. The concentrations of OC were higher than EC at three sampling sites, and the average concentrations of EC (11.31 µg m$^{-3}$) at site 3 were higher than the other two sites. In this study, OC/EC ratios ranged from 9.1 to 12.4 with a daily mean value of 10.8 during HPE, which suggested that carbonaceous PM constituents might be from the same sources. The total concentration of WSII at three sites ranged from 72.2 to 100.0 µg m$^{-3}$ with a mean of 84.3 µg m$^{-3}$. The dominant species were NO$_3^-$, SO$_4^{2-}$, NH$_4^+$, and Cl$^-$, accounting for 88.39% of the total WSII mass of PM$_{2.5}$. The most abundant element was Na with an average mass concentration of 41.5, 37.1, and 38.1 µg m$^{-3}$ during HPE, while the mean value was 32.2 µg m$^{-3}$ during CD, meanwhile the eleven trace elements (V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Ba and Pb) accounted for a small part (1.76%, 1.63% and 1.86%) of the total inorganic element.

In addition, the average wind speed was 7.88 km h$^{-1}$ and 13.7 km h$^{-1}$ during HPE and CD, a relative humidity during HPE was higher than the data during CD, and the average relative humidity was 70.1% and 60.3%, respectively, which suggested a high relative humidity and low wind speed was found to favor the formation of secondary inorganic ions and accelerate hygroscopic growth. The back-trajectories analysis of three sites indentified almost similar transport pathways, and the potential source areas for PM$_{2.5}$ of Shijiazhuang were Beijing – Tianjin region and Shandong Province. The results obtained from this study are expected to be useful for enlarging degree of pollution prevention and treatment in Hebei Province to improve air quality at Shijiazhuang.

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**SUPPLEMENTARY MATERIAL**

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

**REFERENCES**


