Characteristics of PM$_{2.5}$ and Assessing Effects of Emission–Reduction Measures in the Heavy Polluted City of Shijiazhuang, before, during, and after the Ceremonial Parade 2015

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ABSTRACT

The measurement of PM$_{2.5}$ was conducted from 15th August to 17th September, 2015 in Shijiazhuang, China, covering the period of a ceremonial parade. The PM$_{2.5}$ concentrations and the major chemical components were analyzed. The concentrations of PM$_{2.5}$ was 26.5 µg m$^{-3}$ during control, which were 57.0% and 51.1% lower compared to before and after control, respectively. The lowest concentrations of elements and water-soluble ions were also found during control with a decreasing trend of 31.1%–44.2%, and 57.1%–64.2%, respectively. Two typical pollution episodes characterized by significantly elevated PM$_{2.5}$ concentration were found during no control due to the combination of no emission-reduction measures and unfavorable weather conditions. The mass percentage of secondary inorganic ions was larger during no control (38.1%–40.3%), pointing to the strong contribution of atmospheric chemical processes. The NO$_3^–$/SO$_4^{2–}$ ratios were 0.85, 0.94, and 0.85 before, during, and after control, respectively, and the elevated ratios during control indicate a greater proportion of the PM$_{2.5}$ originated from vehicle exhaust. The WRF-CMAQ modeling system was also used to assess the effectively of emission reduction measures and weather conditions. The results indicated that the PM$_{2.5}$ concentration increased by 21.6% and 32.1% if no emission-reduction measures were taken and weather conditions in 2014 were used.

Keywords: PM$_{2.5}$ pollution; Element; Water-soluble ions; Emission control assessment; Simulation modeling.

INTRODUCTION

As the capital city of Hebei province, Shijiazhuang has experienced rapid economic development, population expansion and urbanization during the last few decades, with high PM$_{2.5}$ (i.e., particles with an aerodynamic diameter of $\leq$ 2.5 µm) concentration. At present, coal is the primary fuel in Hebei province and emissions of PM$_{2.5}$ are much higher than in other areas, leading to a rapid deterioration of air quality in Shijiazhuang (Yao et al., 2016). According to the 2015 air quality status reports of 74 cities in China (MEP, 2016), Shijiazhuang city was ranked 8th among the 10 most polluted cities. The rapid deterioration of air quality in recent years not only leads to a concern due to its adverse health effects, but also triggers the government to tackle the serious air quality problem especially PM$_{2.5}$ pollution. Therefore, a series of pollution control measures has been adopted by Shijiazhuang government to effectively control regional PM$_{2.5}$ and improve the air quality recently. Compared with 2012, the PM$_{2.5}$ concentrations need to decrease by 33% in 2017 according to “A crucial action plan for the air pollution control of Shijiazhuang” presented by the People’s Government of Shijiazhuang Municipality in 2013. The measures mainly included the optimization and adjustment of energy and industrial structure, comprehensive industrial pollution comprehensive treatment, vehicle exhaust pollution control, and elimination of outdated technology. The PM$_{2.5}$ concentrations had dropped considerably in recent years with the annual average of 157.0 µg m$^{-3}$, 114.1 µg m$^{-3}$, and 89.0 µg m$^{-3}$ in 2013, 2014, and 2015, respectively. Even so, the annual PM$_{2.5}$ concentrations remained above 35 µg m$^{-3}$ compared with 2nd-level air quality standard in China (GB 3095–2012) by a factor of 4.5, 3.3, and 2.5, respectively.

For several years, atmospheric aerosols have received...
considerable attention. PM$_{2.5}$ is one of the significant pollutants with adverse health impacts like premature mortality, lungs and cardiovascular diseases (Silva et al., 2013; Hou et al., 2015), and also has a serious impact on atmospheric visibility and global climate change (Cheng et al., 2011). First of all, PM$_{2.5}$ is not a single molecule but a mixture of many species. The composition of PM$_{2.5}$ is complex, and includes components from various sources such as vehicle emissions, industry, biomass burning, and other human activities. PM$_{2.5}$ contains optically scattering constituents such as SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ products, which are related to the atmospheric precipitation acidity closely. It can affect cloud condensation nuclei which then impacts earth radiation balance (Pathak et al., 2011). Secondly, inorganic element has important influence on human health, although its mass concentration in PM$_{2.5}$ is relatively less. 14 kinds of heavy metals (e.g., Pb and Hg) are considered as the key objectives of prevention and control according to the “Plan for the prevention and control of heavy metal pollution (2010–2015)” was established by Chinese government during the period of “twelfth five-year plan”. Heavy metals can cause illness to human body, even has strong effects of carcinogenic, teratogenic and mutagenic.

Based on these facts, numerous studies on PM$_{2.5}$ have received increasing worldwide attention. These studies have involved PM$_{2.5}$ seasonal variation (Rogula-KozAWSKAS et al., 2014; Masiol et al., 2015), PM$_{2.5}$ components (e.g., elements, water-soluble ions, and carbonaceous) (Zhao et al., 2013; Wen et al., 2016), source apportionments (Tan et al., 2016; Yao et al., 2016), dust storms (Tsai et al., 2006; Wang et al., 2013), haze episodes (Sun et al., 2006; Zhang et al., 2013), size distribution (Yang et al., 2015; Wang et al., 2015d), and epidemiological studies (Dominici et al., 2005; Quan et al., 2011). For instance, a study on size distributions of atmospheric elements and water soluble inorganic ions was carried out during haze period in winter in Beijing, China (Tan et al., 2016). Zhang and Cao (2015) presented a long term datasets including a statistical summary of PM$_{2.5}$ concentrations obtained from one-year monitoring in 190 cities in China, and a remarkable seasonal variability of PM$_{2.5}$ was observed. The principal component analysis model was used by Wang et al. (2015a) and the vehicle emission was the major contributor to the carbonaceous components of PM$_{2.5}$, accounting for 63.0% of total mass in summer in Beijing. The effectiveness of the pollution control measures on the air quality was also reported. A coupled MM5-CMAQ modeling system was employed by Zhou et al. (2012) to assess the effects of different restriction policies implemented during and after the 2008 Olympic Games. Liu et al. (2013) applied observation data, emission reduction measures, and air quality simulations to analyze the relationship between emissions and concentrations of pollutants during the Asian Games in Guangzhou.

These studies could provide scientific support to further researches such as global climate change, particulate pollutant formation, and pollution control. However, the research on overall analyses for PM$_{2.5}$ chemical characteristics and effectiveness of the control measures and weather conditions has been limited. What is more, the Ceremonial Parade of the 70th Anniversary of the Chinese Anti-Japanese War and the World Anti-Fascist War (ceremonial parade) was held in 3rd September in Beijing, China, 2015. To improve the air quality during the ceremony, a series of effectively emission-reduction measures had been carried out to guarantee the air pollution controlled and lessened. As one of the pollution emission reduction city, Shijiazhuang also adopted a series of strict measures to control emission sources. Emission reduction measures of atmospheric pollutants in view of the major events in China are relatively rare, which had provided an invaluable opportunity for environmental protection workers to study the relationship between PM$_{2.5}$ and emission reduction.

A comprehensive investigation focusing on PM$_{2.5}$ components and reduction effect during this period in Shijiazhuang was desirable. Therefore, observations of ambient PM$_{2.5}$ samples were conducted to discuss the characteristics from 15th August to 17th September, 2015 in Shijiazhuang, China. The Weather Research and Forecasting model (WRF) and the air quality model Model-3/Community Multiscale Air Quality (CMAQ) were also applied to assess the influence of emission-reduction measures and weather conditions. The objectives of this study mainly include: (1) analyzing the pollution levels of PM$_{2.5}$, elements, and water soluble inorganic species before, during and after the emission-reduction measures; (2) analyzing the reason of pollution episodes during the sampling period; (3) assessing the effectively of emission reduction measures and weather conditions. The results gained from this study are expected to be helpful to understand the components of PM$_{2.5}$ and policy making in Shijiazhuang.

**METHODS**

*The Monitoring Locations and PM$_{2.5}$ Sampling*

Shijiazhuang (113.50°E–115.33°E, 37.45°N–38.78°N) is located in the western part of the North China Plain, and surrounded by the Taihang Mountains to the west. Shijiazhuang belongs to the monsoon climate of medium latitudes, and prevailing northwest wind in winter, and southeast wind in summer. The annual average air humidity is 65%, and annual total precipitation is ranged from 401.1 to 752.0 mm. It possesses a population over 10.5 million in 2013 and a land area about 15,848 km$^2$. The Environmental Monitoring Center (EMC) site located in the urban area of Shijiazhuang was selected for collecting PM$_{2.5}$ samples (Fig. 1). The sampling site is ~20 meters above the ground, on the rooftop of an office building, where the atmospheric mixing reflects the condition of regional atmospheric pollution. This site is surrounded by offices and residential buildings, while two roads with moderate traffic are located 200 m and 280 m away in the west and the south, respectively. As an urban sampling location, the EMC site represents a mixed commercial, residential and traffic condition.

In order to analyze the diurnal variation of PM$_{2.5}$, samples were collected on 31 days from 15th August to 17th September, 2015 (note: samples on 4th to 6th September missed due to mechanical failure). PM$_{2.5}$ sampler (Wuhan Tianhong Instruments Co., Ltd.) was employed to collect daily PM$_{2.5}$
samples (from 9:00 a.m. to 9:00 a.m.) at the flow rate of 100 L min⁻¹. The samples were collected on 90-mm quartz filters (Whatman Inc Maidstone, UK) for analysis of elements and water-soluble ions. Filters were equilibrated at 20 ± 5°C and a relative humidity of 40 ± 2% for 48 h in a clean room before and after sampling. Filters were placed in zip lock bags immediately after sample collection, and stored in a refrigerator at about 4°C until chemical analysis to avoid the evaporation of volatile components. The PM2.5 mass was weighed using an electronic micro balance (accuracy of 0.01 mg) (Sartorius TB-215D, Germany). A total of 30 valid PM2.5 samples were collected during the sampling period and sent to laboratory for analysis. Additionally, meteorological parameters, including ambient temperature, relative humidity, wind speed, wind direction, atmospheric pressure and precipitation during the sampling periods were obtained from the Weather Underground website (www.wunderground.com). The concentrations of gaseous pollutants, including O₃, NO₂, SO₂, and CO were obtained from Shijiazhuang Municipal Environmental Protection Bureau which were measured in the Urban Century Park Station. The station was only about 40 meters away in the north side of the sampling site.

Chemical Analysis and Quality Control

One-fourth of quartz filters was digested at 170°C for 4 h in high-pressure teflon digestion vessel with 3 mL concentrated HNO₃, 1 mL concentrated HClO₄, and 1 mL concentrated HF (Han et al., 2007). After cooling, the solutions were dried, and then diluted to 10 mL with distilled-deionized water. Finally, the concentrations of 23 elements (Na, Mg, Al, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, Sb, Ce, Eu, and Pb) were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, 7500a, Thermo).

One-fourth of quartz filters was extracted ultrasonically by 10 mL distilled-deionized water and oscillated for 40 min in supersonic cleaner. The concentrations of 10 water-soluble ions (F⁻, Cl⁻, NO₃⁻, SO₄²⁻, NO₂⁻, Na⁺, NH₄⁺, K⁺, Ca²⁺, and Mg²⁺) were determined by Ion Chromatograph (IC, Metrohm 861 Advanced Compact IC). More detailed water-soluble ions analytical procedures were given elsewhere (Wang et al., 2015b).

The cutting head of atmospheric particulate sampler was cleaned by alcohol before PM2.5 sampling. The flow rate of the sampler was calibrated before sample collection to ensure the deviation of flow rate of the sampling system was within 5%. The blank filters were analyzed using the same methods as described above and the sample results were corrected by the average blank concentrations. The standard solution of elements and water-soluble ions were also analyzed using the same methods. A calibration curve of each target compound was performed and the correlation coefficient values were all above 0.999, which showed the good linearity between the response value and the corresponding concentrations.

WRF-CMAQ Modeling System

Emission Reduction in Different Control Strategies

To achieve the goal of “blue ceremony”, a series of effectively emission-reduction measures had been carried out from 28th August to 4th September by Beijing and neighbouring regions (e.g., Tianjin, Hebei, Shandong, Shanxi, Henan, and Inner Mongolia). Take Shijiazhuang for example, coal-fired facilities halted from production or cut their productions by 30%. Vehicles were restricted based on the odd-even day operation from 7 a.m. until 21 p.m. in the urban area of Shijiazhuang. What is more, a total of 239 construction sites have discontinued. Based on the above emission-reduction plan obtained from Environmental Protection Ministry of Shijiazhuang, the emission coefficients method was applied to calculate the emissions of pollutants. Compared to the original emission inventory, the emission reduction rates were 27.7%, 22.3%, 21.6%, and 34.6% for SO₂, NOₓ, VOCs, and PM₂.₅, respectively in Shijiazhuang. The original emission inventory was mainly obtained from local environmental protection bureaus or administrations. The data was calculated based on the categories of activities
and their emission coefficients by our colleagues. More detailed descriptions of the complete emission inventory can be found in previous works published by our colleagues (Cheng et al., 2012; Lang et al., 2013; Wen et al., 2016).

Modeling Description and Application

The WRF-CMAQ modeling system was used to simulate the PM$_{2.5}$ concentration in Shijiazhuang in this study, which has been widely used in China (Wen et al., 2016). The initial and boundary conditions for the WRF simulation were prepared using the 1 × 1 resolution final global tropospheric analyses data (FNL) which was produced by National Centers for Environmental Prediction’s (NCEP) Global Forecast System (GFS). In this study, a three-level nested-grid architecture was employed for the implementation of the WRF-CMAQ modeling system (Fig. 1). Modeling domain 1 covered most areas of northeastern China with a spatial resolution of 27 km × 27 km. Modeling domain 2 covered Beijing and its surrounding regions with a 9 km × 9 km spatial resolution. Modeling domain 3 covered Shijiazhuang with a spatial resolution of 3 km × 3 km (Fig. 1). Vertically, 28 sigma levels were designed in the WRF simulation. The WRF outputs from 28 vertical levels were transformed into 14 levels with the format required by the CMAQ model using the Meteorology Chemistry Interface Processor (MCIP). The CB05 (Carbon Bond mechanism) was chosen as the gas-phase chemistry mechanism.

The simulation target period was 28th August to 3rd September, 2015 corresponding to the control period. And two scenarios were simulated using a zero-out method to calculate the effect of emission-reduction measures to PM$_{2.5}$ concentrations in Shijiazhuang, including the Zero Emission Reduction Scenario (ZERS) and the Emission Reduction Scenario (ERS). The ZERS was corresponding to the base scenario under which the WRF-CMAQ model was run using the original emission inventories. In terms of the ERS, the scenario corresponds to the situations where the emissions from Shijiazhuang and surrounding regions were set to emission reduction inventories. In addition, the same period in 2014 was also chosen for investigating the meteorological effects with the same emission reduction inventories.

RESULTS AND DISCUSSION

PM$_{2.5}$ Characteristics during Sampling Period

The PM$_{2.5}$, O$_3$, NO$_2$, and SO$_2$ concentrations during sampling period were summarized in Fig. 2. The sampling days were divided based on the emission-reduction measures, into before control (15th–27th August), during control (28th August–3rd September), and after control (7th–17th September). The average daily PM$_{2.5}$ concentration ranged from 33.9 to 156.2 µg m$^{-3}$ with an average of 61.6 µg m$^{-3}$ before the control period. During control, this was reduced to 6.0 to 46.2 µg m$^{-3}$ with an average of 26.5 µg m$^{-3}$. After the control period, the daily PM$_{2.5}$ concentration ranged from 8.7 to 111.0 µg m$^{-3}$ with an average of 54.1 µg m$^{-3}$. Thus, the average daily PM$_{2.5}$ concentration during control demonstrated a decreasing trend obviously with 57.0% compared to the period before control. Compared with the period after control, the PM$_{2.5}$ concentration were 51.1% lower during control, which might due to that the emission-reduction measures were cancelled.

The average daily PM$_{2.5}$ concentration should be less than 75 µg m$^{-3}$ for 2nd-level air quality standard in China (GB 3095–2012). It was found that the daily PM$_{2.5}$ concentrations
all meet the standard during control. However, the time with PM$_{2.5}$ exceeding this limitation value accounted for 15.4% and 18.2% of the total number of sampling days before and after control, respectively.

**Pollution Episodes during Sampling Period**

In recent years, the frequent outbreaks of haze episodes over Beijing-Tianjin-Hebei Region of China have drawn public attention. Shijiazhuang suffered two typical pollution episodes, characterized by significantly elevated PM$_{2.5}$ concentration during the sampling period (Fig. 2). The first occurred during 16$^{th}$ to 18$^{th}$ August (before control) and the second during 12$^{th}$ to 17$^{th}$ September (after control). Fig. 3 displays the meteorological parameters observed at the EMC site to further analyze the reason of PM$_{2.5}$ pollution formation in Shijiazhuang.

During the first episode, the PM$_{2.5}$ concentration in 17$^{th}$ August was 2.4 times higher than that in 16$^{th}$. The elevated levels of PM$_{2.5}$ might be associated with the weather type. Although the wind speed increased from 2.2 m s$^{-1}$ in 16$^{th}$ to 3.0 m s$^{-1}$ in 17$^{th}$, the humidity also rises apparently (Fig. 3). What is more the atmosphere controlled by a large-scale uniform pressure field in 17$^{th}$ August according to the meteorological data obtained from the Meteorological Information Comprehensive Analysis and Process (MICAPS) system of China Meteorological Administration (Fig. 4(a)). Inversion layers suppress the vertical dispersion of PM$_{2.5}$ due to lower mixing depth under the control of uniform pressure field, which is conducive to the accumulation of pollutants. The NO$_2$, SO$_2$, and CO concentrations in 17$^{th}$ August increased by 43.1%, 17.5%, and 88.6%, respectively compared to that in 16$^{th}$. The reason was that the particles can grow more easily in high humidity and pollution episodes, than on clear days. Then, the atmosphere controlled by obviously pressure gradient in 18$^{th}$ and the diffusion conditions was better (Fig. 4(b)). The PM$_{2.5}$, NO$_2$, SO$_2$, and CO concentrations decreased by 54.4%, 51.2%, 85.9%, and 54.2%, respectively compared to that in 17$^{th}$.

During the second episode, the PM$_{2.5}$ concentrations increased gradually from 12$^{th}$ to 17$^{th}$ September, with the highest value of 111.0 µg m$^{-3}$. First of all, the average humidity was also increased gradually as a whole from 44% to 67%, and the average wind speed showed a gradual decreasing from 5.3 to 1.4 m s$^{-1}$ (Fig. 3). Secondly, the atmosphere controlled by a large-scale uniform pressure field again in 17$^{th}$ September (Fig. 5), leading to a relatively

![Fig. 3. Meteorological condition in Shijiazhuang during the sampling period.](image-url)
Fig. 4. Surface pressure in Shijiazhuang at 17:00 on August 17\(^{th}\) (a) and 18\(^{th}\) (b), 2015 (the star denote the PM\(_{2.5}\) sampling site).

Stagnant atmosphere. Stable conditions near the surface during that time also would limit the diffusion of pollutants. Thirdly, the emission-reduction measures were cancelled. It was also observed that the SO\(_2\), NO\(_2\), CO, and O\(_3\) concentrations in 17\(^{th}\) increased by 54.4\%, 51.2\%, 85.9\%, and 54.2\%, respectively compared to that in 12\(^{th}\). The condition from the three aspects is conducive to photochemical reaction which could result in secondary pollution (Pachauri \textit{et al.}, 2013).

During the control period, no heavy pollution occurred, and the PM\(_{2.5}\) concentration was just 7.2 \(\mu\)g m\(^{-3}\) in 3\(^{rd}\) September. The lower PM\(_{2.5}\) concentration during control has also a clear relationship with emission sources and meteorological condition. From the emission sources perspective, vehicles were restricted based on the odd-even day operation during control. Correspondingly, a significantly decreased rate of NO\(_2\) and CO had dropped by 48.3\% and 44.6\%, respectively during control compared to before control. Those were the main pollutants of vehicle emissions and in accordance with the emission-reduction measures of vehicles during this period. Secondly, as many as 834 industrial
enterprises were discontinued and limited production. Coal-fired facilities had reduced emissions by more than 30% by reducing the production load. Correspondingly, a significantly decreased rate of SO2 was also found during control (48.1%). Thirdly, in addition to local emissions, the cities of the BTH region were susceptible to the influence of regional pollution transfer for the special geographical position. Thus, the transport of pollutants seems another highlighted factor in influencing PM2.5 concentrations. The numerical simulation method was applied by Lang (2013) to study the PM2.5 contribution to Shijiazhuang from surrounding cities. The result demonstrated that Shijiazhuang was prone to influenced by long transportation sources and the contribution rate of peripheral transmission was about 30%. Therefore, concentrations of PM2.5 and gaseous precursors decreased significantly due to the emission-reduction measures carried out by neighbouring regions (e.g., Baoding, Xingtai, and Handan). From the meteorological condition perspective, the atmosphere also controlled by obviously pressure gradient during control in Shijiazhuang and the diffusion conditions was better (Fig. 6). This trend was mainly result from the implementation of air pollution control policies during control, and the air quality was somehow improved as a whole.

**Elements Characteristics during Sampling Period**

The mean concentrations of 23 elements during three sampling periods were given in Table 1. The percentages of total detected elements in PM2.5 were 6.5%, 8.4%, and 5.9% before, during, and after control, respectively. As expected, the crustal elements (i.e., Ca, Al, Na, Mg, and Fe), mainly from soil or construction dust, constituted the largest fraction, accounting for 84.8% to 87.5% of total detected elements. Ca was the most abundant element of the crustal elements, which contributed 25.8% to 33.1% of the total detected elements. Fe is often considered crustal elements as a result of emissions from mineral dust. A higher correlation coefficient was found among the five species (0.68–0.93) during the three periods, reflecting the crustal sources. The lowest concentrations of the crustal elements all appeared during control, which might be due to the measures of road sweeping and construction sites shutting down. What is more, a lot of buildings were under construction or demolition before and after control also made a contribution to the concentration of crustal elements.

The soil-related elements such as Si, Al, Fe, and Ca have been used to estimate the fraction of the crustal contribution by summing the oxides of the major soil-associated elements (i.e., Al2O3, SiO2, CaO, FeO, Fe2O3, and TiO2), and the calculation can be described as follows (Kim et al., 2001):

\[
[S_{\text{soil}}] = 2.20[\text{Al}] + 2.49[\text{Si}] + 1.63[\text{Ca}] + 2.42[\text{Fe}] + 1.94[\text{Ti}]
\]  

(1)

The concentration of Si was estimated by 4 times of Al due to the lack of standard solution (Yuan et al., 2008). The concentrations of soil dust were 13.6 µg m⁻³, 5.7 µg m⁻³, and 9.6 µg m⁻³ before, during, and after control, respectively. In contrast, trace elements (i.e. Cr, Mn, Ni, Cu, Zn, As, and Pb) accounted for a small part but noticeable percentages of the total detected elements with 11.0%, 11.3%, and 13.9% before, during, and after control, respectively. The higher concentrations of the soil dust and trace elements appeared before and after control, likely attributed to the combination of floating dust weather and increased anthropogenic emissions in Shijiazhuang. Heavy metals can cause serious bodily damage, and concentration standard have not given in ambient air quality standards. The sum concentration of Mn, Zn and Cu was found to contribute about 0.43%–0.56% of the total PM2.5 mass concentration.
Table 1. Average concentrations of major components in PM$_{2.5}$ during sampling periods (µg m$^{-3}$).

<table>
<thead>
<tr>
<th>Species</th>
<th>Before control</th>
<th>During control</th>
<th>After control</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average ± SD</td>
<td>Average ± SD</td>
<td>Average ± SD</td>
</tr>
<tr>
<td>Elements</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>0.48 ± 0.39</td>
<td>0.42 ± 0.35</td>
<td>0.58 ± 0.38</td>
</tr>
<tr>
<td>Mg</td>
<td>0.25 ± 0.21</td>
<td>0.16 ± 0.01</td>
<td>0.17 ± 0.11</td>
</tr>
<tr>
<td>Al</td>
<td>0.81 ± 0.50</td>
<td>0.29 ± 0.08</td>
<td>0.55 ± 0.23</td>
</tr>
<tr>
<td>Ca</td>
<td>1.32 ± 1.21</td>
<td>0.60 ± 0.15</td>
<td>0.83 ± 0.35</td>
</tr>
<tr>
<td>Ti</td>
<td>0.04 ± 0.02</td>
<td>0.03 ± 0.03</td>
<td>0.04 ± 0.03</td>
</tr>
<tr>
<td>Mn</td>
<td>0.04 ± 0.02</td>
<td>0.03 ± 0.03</td>
<td>0.04 ± 0.03</td>
</tr>
<tr>
<td>Fe</td>
<td>0.62 ± 0.28</td>
<td>0.44 ± 0.23</td>
<td>0.60 ± 0.41</td>
</tr>
<tr>
<td>Cu</td>
<td>0.03 ± 0.02</td>
<td>0.02 ± 0.01</td>
<td>0.03 ± 0.03</td>
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<tr>
<td>Zn</td>
<td>0.20 ± 0.11</td>
<td>0.10 ± 0.07</td>
<td>0.22 ± 0.16</td>
</tr>
<tr>
<td>As</td>
<td>0.02 ± 0.01</td>
<td>0.01 ± 0.01</td>
<td>0.02 ± 0.02</td>
</tr>
<tr>
<td>Pb</td>
<td>0.15 ± 0.12</td>
<td>0.09 ± 0.05</td>
<td>0.13 ± 0.09</td>
</tr>
<tr>
<td>Other elements</td>
<td>0.02 ± 0.01</td>
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<tr>
<td><strong>Total elements</strong></td>
<td><strong>3.98 ± 2.62</strong></td>
<td><strong>2.22 ± 1.75</strong></td>
<td><strong>3.22 ± 1.61</strong></td>
</tr>
<tr>
<td>Water-soluble ions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>0.09 ± 0.09</td>
<td>0.08 ± 0.01</td>
<td>0.05 ± 0.04</td>
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<tr>
<td>Cl$^-$</td>
<td>3.40 ± 1.67</td>
<td>0.99 ± 0.77</td>
<td>2.50 ± 1.51</td>
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<tr>
<td>NO$_2^-$</td>
<td>0.03 ± 0.03</td>
<td>0.03 ± 0.03</td>
<td>0.03 ± 0.03</td>
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<tr>
<td>NO$_3^-$</td>
<td>8.30 ± 5.44</td>
<td>2.78 ± 2.27</td>
<td>6.87 ± 4.95</td>
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<tr>
<td>SO$_4^{2-}$</td>
<td>9.80 ± 5.99</td>
<td>2.96 ± 2.31</td>
<td>8.08 ± 5.49</td>
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<tr>
<td>Na$^+$</td>
<td>0.70 ± 0.17</td>
<td>0.47 ± 0.30</td>
<td>0.81 ± 0.47</td>
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<td>NH$_4^+$</td>
<td>6.72 ± 4.65</td>
<td>2.42 ± 2.01</td>
<td>5.64 ± 4.32</td>
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<tr>
<td>K$^+$</td>
<td>1.62 ± 0.61</td>
<td>0.65 ± 0.73</td>
<td>1.67 ± 1.75</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.76 ± 0.19</td>
<td>0.39 ± 0.34</td>
<td>0.59 ± 0.32</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>1.60 ± 0.61</td>
<td>1.04 ± 0.10</td>
<td>1.28 ± 0.35</td>
</tr>
<tr>
<td><strong>Total ions</strong></td>
<td><strong>33.02 ± 16.66</strong></td>
<td><strong>11.82 ± 8.65</strong></td>
<td><strong>27.52 ± 18.29</strong></td>
</tr>
</tbody>
</table>

due to their greater presence in smelters and metallurgical industries. The concentration of Pb was 0.15 ± 0.12 µg m$^{-3}$, 0.09 ± 0.05 µg m$^{-3}$, and 0.13 ± 0.09 µg m$^{-3}$ in PM$_{2.5}$ before, during, and after control, respectively. Correspondingly, As was 0.02 ± 0.01 ng m$^{-3}$, 0.01 ± 0.01 ng m$^{-3}$, and 0.02 ± 0.02 ng m$^{-3}$ in PM$_{2.5}$. Pb and As are enriched in Chinese coal, and a large amount of coal was combusted for industrial processes during and after control, which leading to a higher concentration compared to that during control. However, other elements contented in PM$_{2.5}$ were scarce.
Water-Soluble Ions Characteristics during Sampling Period

The monitoring results of water-soluble ions in PM$_{2.5}$ during three periods were presented in Table 1. The average daily concentrations of total water-soluble ions (TWSI) were $33.0 \pm 16.7 \mu g \ m^{-3}$, $11.8 \pm 8.7 \mu g \ m^{-3}$, and $27.5 \pm 18.3 \mu g \ m^{-3}$ before, during and after the control period, respectively. Thus, the TWSI concentration during control demonstrated a decreasing trend with 64.2% obviously than the period before control. Compared with the period after control, the TWSI concentration were 57.1% lower during control. This demonstrated might due to the emission-reduction measures as well as the better diffusion conditions during control.

The concentrations of secondary inorganic ions (SIA, SIA = SO$_4^{2-}$ + NO$_3^-$ + NH$_4^+$) represented a significant component in water-soluble ions, and the concentration was ranked in the following order as SO$_4^{2-}$ > NO$_3^-$ > NH$_4^+$. The SIA accounted for 40.3%, 30.8%, and 38.1% of the total mass of PM$_{2.5}$ before, during and after control, respectively. The larger percentage indicated the relative strong contribution of atmospheric chemical processes before and after control. Furthermore, as the most important photochemical oxidant, the O$_3$ concentration was 68.8 $\mu g \ m^{-3}$ and 67.4 $\mu g \ m^{-3}$ before and after control, respectively, which was 1.7 and 1.6 times higher than that during control. The higher O$_3$ concentration could also facilitate the formation of SIA by photochemical oxidation. What is more, the strong correlations ranged from 0.69 to 0.90 between SIA and PM$_{2.5}$ were observed during three periods, indicating that the SIA variations might related to the formation and removal of PM$_{2.5}$.

The emitted SO$_2$, mainly derived from coal burning, are oxidized to SO$_4^{2-}$ aerosols through heterogeneous or homogeneous reaction. As the dominant species in fine particles, a significantly decreased rate of SO$_4^{2-}$ was also found during control with an average of 69.8% and 63.4% compared to before and after control, respectively. NO$_3^-$ was transformed through the photo-oxidation of NO$_2$. A significantly concentration decreased rate of NO$_3^-$ was also found during control with an average of 66.6% and 59.6% compared to before and after control, respectively. That was in accordance with the combined effect of vehicles and industrial enterprises. The emission reduction rates of SO$_2$ was high (27.7%), and a series of measures adopted were conducted by enterprises (e.g., cement, steel, and ceramic) to reduce the pollutants emissions, including stopping production and reducing the production load. Those all made a more significant decrease of SO$_4^{2-}$ than other compositions. The SO$_2$ and NO$_3^-$ concentration after control also had a significant rise with 4.0 and 3.5 times higher compared to control period due to the cancellation of emission-reduction measures, which indicated that the emission reduction of SO$_2$ and NO$_3^-$ had play a remarkable achievement during control.

NH$_4^+$ is formed from the gaseous precursor of NH$_3$ through gas and aqueous phase reaction with acidic species. NH$_4^+$ is primarily emitted from agricultural activities in the atmosphere. The decreased rate of NH$_4^+$ was relatively less with an average of 64.0% and 57.1%, respectively during control compared to no control. The decreasing of NH$_4^+$ was mainly due to the emission-reduction measures of prohibition of open burning and strengthens the breeding livestock and poultry waste disposal. Chemical industries were also considered to be a major source of NH$_3$, and a total of 108 chemical industries were reduced the production load. Additionally, NH$_4^+$ existed in the form of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ in the atmosphere, the decrease of SO$_4^{2-}$ and NO$_3^-$ result in the decrease of NH$_4^+$ concentration.

In addition to the three inorganic particles, Ca$^{2+}$ and Mg$^{2+}$, used as an indicator of mineral dust (Shen et al., 2007), were also the important water-soluble ions and couldn’t be ignored. In our study, the sum concentration of Mg$^{2+}$ and Ca$^{2+}$ in PM$_{2.5}$ were 1.4 $\mu g \ m^{-3}$ during control, which were 39.2% and 23.4% lower than those before and after control, respectively. That was reasonably attributed to the emission-reduction measures. For instance, the construction sites take measures to restrain dust rising such as sprinkler and cover, increase the frequency of street sweepings and road washing, strengthen management and supervision of road dust. Additionally, traffic restriction could make the decrease of road dust, leading a relatively lower Mg$^{2+}$ and Ca$^{2+}$ concentration. Research indicated that Na$^+$ and Cl$^-$ were the characteristic component of sea salt, and the mass concentration ratio of Cl$^-$ and Na$^+$ (ratio = Cl$^-$/Na$^+$) was 1.16 (Tsitouridou and Samara, 1993). The concentration of Na$^+$ had few differences during three periods. The concentration of Cl$^-$ was lower during control, with the decreased rate of 70.8% and 60.2% compared to before and after the control, respectively. The annual daily ratios were 4.9, 2.1, and 3.1, respectively before, during, and after control, which indicated that Na$^+$ in PM$_{2.5}$ significantly affected by human activities obviously (e.g., coal combustion). Shijiazhuang is a typical inland city and away from the ocean, Cl$^-$ would also be released in the process of coal combustion (Wang et al., 2005). The un-eliminated boilers with 10 steam-tons and other burning coal facilities were temporarily closed. The first, the second and the third industry involved in coal-fired facilities reduced pollutant emissions by more than 35% by stopping production, reducing the production load, and other measures. Therefore, the emission-reduction measures of coal combustion (e.g., coal-fired power plants and coal-fired boiler) made the obvious concentration differences of Cl$^-$ during different periods. K$^+$ is enriched in the aerosol as a result of biomass burning (Raveendran et al., 1995). The proportion of K$^+$ also showed obvious variation, and the concentration were increased by 59.6% and 60.7% during before and after control compared to during control, respectively, which may be attributed to the burning of wheat straw and maize stalks. The concentrations of other water-soluble ions such as F$^-$ and NO$_3^-$ were lower in atmospheric particulate matter with the percentage below 0.3%.

The NO$_3^-$/SO$_4^{2-}$ Ratios during Sampling Period

The NO$_3^-$/SO$_4^{2-}$ ratios higher than 1.0 or not is generally used to estimate the contribution of stationary source and vehicle source to sulfur and nitrogen in the atmosphere (Yao et al., 2002; Ye et al., 2003) and this method has been adopted by many researchers (Xiao and Liu, 2004; Wang et al., 2006).
Higher \( \text{NO}_3^-/\text{SO}_4^{2-} \) ratios were ascribed to the pre-pollutants of vehicle sources over stationary sources of pollutants (Wang et al., 2005). Fig. 4 presents the variation of observed \( \text{NO}_3^-/\text{SO}_4^{2-} \) ratios during the three periods. It could be found that the daily average \( \text{NO}_3^-/\text{SO}_4^{2-} \) ratios were 0.85, 0.94, and 0.85 before, during, and after control, respectively, indicating that stationary sources accounted for an important emission source for the formation of PM\(_{2.5}\) pollution in Shijiazhuang. Elevated \( \text{NO}_3^-/\text{SO}_4^{2-} \) ratios during control indicate that a greater proportion of the PM\(_{2.5}\) originated from vehicle exhaust compared with no control, which might due to a series of emission-reduction measures on SO\(_2\). In terms of coal-burning, the reduction of pollutants were over 30% by adopting a series of measures, such as stopping production, reducing the production load, strengthen operation and management of pollution control facilities. In terms of industrial emissions control, the reduction of pollutants of elevated point sources, including steel, coking, cement, glass, and ceramic industries, were over 50%. However, the measures on the main source for NO\(_2\) emission were restricted based on the odd-even day operation for vehicles. Therefore, the SO\(_2\) concentration decreased by 61.8% during control compared to before control, by comparison, NO\(_2\) decreased by 50.6%. Those were all lead to a relatively higher \( \text{NO}_3^-/\text{SO}_4^{2-} \) value during control.

Compared the \( \text{NO}_3^-/\text{SO}_4^{2-} \) ratios observed from this work and other cities in China, the value were 1.87 and 1.27, respectively in Beijing and Tianjin (Zhao et al., 2013), which was higher than that in Shijiazhuang obviously (Fig. 7). The difference of the value was associated with the growth of the rapid increase of vehicle population, and the vehicle population was 5.61 and 2.85 million in Beijing and Tianjin in 2015, respectively, which was 2.4 and 1.2 times higher than that in Shijiazhuang (2.32 million). Atmospheric pollution caused by vehicle exhaust was gradually increased, indicating the greater contribution of vehicle source to NO\(_2\) and SO\(_2\). However, the \( \text{NO}_3^-/\text{SO}_4^{2-} \) ratios was 0.28, 0.38, 0.44, and 0.87 in Chengde (Zhao et al., 2013), Jinan (Gao et al., 2011), Xiamen (Zhang et al., 2012), and Xi’an (Wang et al., 2015c), respectively, and the small value could be explained by the extensive burning of coal for industry. The industrial emission of SO\(_2\) was fewer in most developed countries, leading a higher \( \text{NO}_3^-/\text{SO}_4^{2-} \) ratios in atmospheric particulates. For instance, the value was up to 1.85 in Seoul megacity, where little coal was burned (Kim et al., 2000).

**The Effect of Emission Control Assessment**

A total number of 36 grid cells in the urban area of Shijiazhuang was selected within modeling domain 3 to assess the modeling performance under ZERS. The average simulated PM\(_{2.5}\) concentrations within the grid cells containing six monitoring stations was calculated to compare with the average observation results during sampling period. Fig. 8 presents the scatter plots of the simulated PM\(_{2.5}\) concentrations versus the observation results. It could be found that the correlation coefficient (CC) and normalized mean error (NME) between the simulated and observed concentrations were 0.81 and 32.5%, respectively. Meanwhile, the simulated concentrations of \( \text{SO}_4^{2-} \), \( \text{NO}_3^- \), and \( \text{NH}_4^+ \) within the grid cell containing the EMC sampling site were also compared with the observation results from the monitoring station. The CCs were 0.70, 0.63, and 0.59 for \( \text{SO}_4^{2-} \), \( \text{NO}_3^- \), and \( \text{NH}_4^+ \), respectively. Correspondingly, the NMEs were 35.1%, 39.5%, and 36.3%. The NMEs of
secondary inorganic ions were relatively larger compared to PM$_{2.5}$, which might be affected by the uncertainty of emission inventories. Also, considering the inherent uncertain nature of meteorological and air quality simulation, the modeling performance of the WRF-CMAQ for simulating PM$_{2.5}$ concentrations in Shijiazhuang was acceptable (Chen et al., 2007; Wang et al., 2011).

The WRF/CMAQ model was used to analysis the air quality during control in the urban area of Shijiazhuang. The simulation result of ERS indicated that the PM$_{2.5}$ concentration were 30.2 µg m$^{-3}$ during control with the emission reduction inventories. However, PM$_{2.5}$ concentration increased by 21.6% if no emission-reduction measures were taken. The concentration difference indicated that the stringent air quality restrictions implemented during the “ceremony parade” were successful for “blue ceremony”. The contribution of vehicle emissions to PM$_{2.5}$ pollution during control was also analyzed. The Vehicle Emission Reduction Scenario (VERS), which the emissions from vehicles were set to zero, was simulated by the WRF/CMAQ model. The simulation result of VERS indicated that the PM$_{2.5}$ concentration were 26.4 µg m$^{-3}$ during control. The concentration difference between VERS and ERS indicated that the contribution of vehicle emissions to PM$_{2.5}$ pollution was 12.6% during control. The contribution from the numerical models was relatively small due to that only minor portion of secondary organic aerosol transformed from vehicle to VOCs (Jing et al., 2016).

The simulation results of ERS during the same period in 2014 indicated that the weather conditions caused an increasing of average PM$_{2.5}$ concentration by 32.1% when compared to the results of 2015. However, the average PM$_{2.5}$ concentration was reduced by 123.9% during the same period in 2014 comparing to 2015. It can be concluded that the favorable weather conditions was beneficial for the improvement of the air quality to a certain extent during control in 2015. In view of this, meteorological conditions during the same period in 2014 and 2015 were analyzed. The average wind speed was 2.0 m s$^{-1}$ in 2014, which was below the value in 2015 (2.6 m s$^{-1}$). On the contrary, the average visibility in 2015 (7.0 km) was higher than that in 2014 (4.5 km). Moreover, Shijiazhuang mainly blew easterly winds during the same period in 2014, and the frequency of wind direction (ENE, E, and ESE) was 33%, which was higher than that in 2015 (16%) (Fig. 9). Taihang Mountain in the west would restrict the dispersion of pollutants leading to buildup of pollutant levels.

CONCLUSIONS

PM$_{2.5}$ samples were measured in the suburban area of Shijiazhuang before, during and after the ceremony 2015. The average daily PM$_{2.5}$ concentration was 26.5 µg m$^{-3}$ during control and demonstrated a decreasing trend obviously with 57.0% and 51.1% compared to the period before and after control, respectively. Two typical pollution episodes characterized by significantly elevated PM$_{2.5}$ concentration were also found during no control due to the combination of no emission-reduction measures and unfavorable weather conditions. However, no heavy pollution occurred during control. The major chemical components in PM$_{2.5}$ including 23 elements and 10 water-soluble ions were also analyzed in this study. The total detected elements in PM$_{2.5}$ were 6.5%, 8.4%, and 5.9% before, during, and after control, respectively. Correspondingly, the concentrations of calculated soil dust were 13.6 µg m$^{-3}$, 5.7 µg m$^{-3}$, and 9.6 µg m$^{-3}$, respectively. The total water-soluble ions (TWSI) concentration during control were 64.2% and 57.1% lower obviously compared to the period before and after control, respectively. The secondary inorganic ions (SIA) was major component in water-soluble ions, accounting for 40.3%, 30.8%, and 38.1% of the total PM$_{2.5}$ before, during and after control, respectively. The larger percentage indicated the relative strong contribution of atmospheric chemical
processes before and after control. The NO$_3^-$/SO$_4^{2-}$ ratios were 0.85, 0.94, and 0.85 before, during, and after control, respectively. And the elevated NO$_3^-$/SO$_4^{2-}$ ratios during control indicate that a greater proportion of the PM$_{2.5}$ originated from vehicle exhaust compared with no control due to a series of emission-reduction measures on SO$_2$. The WRF-CMAQ modeling system was also used to assess the effectively of emission reduction measures and weather conditions. The results indicated that the PM$_{2.5}$ concentration increased by 21.6% and 32.1% if no emission-reduction measures were taken and weather conditions in 2014 were used.

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REFERENCES


Wang, Y., Zhuang, G.S., Tang, A.H., Yuan, H., Sun, Y.L.,...


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