Chemical Composition Characteristics of PM$_{2.5}$ in Three Cities in Henan, Central China

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ABSTRACT

The sites of Luoyang, Zhengzhou, and Pingdingshan in Henan, China were selected to investigate the chemical compositions of fine particulate matter (PM$_{2.5}$). A total of 165 PM$_{2.5}$ samples from the three sites were collected from October 2014 to July 2015. Water-soluble inorganic ions, elemental carbon and organic carbon, and other elements in PM$_{2.5}$ were analyzed by ion chromatography, carbon analyzer, and inductively coupled plasma mass spectrometry, respectively. Results showed that the annual average concentrations of PM$_{2.5}$ in the three sites were significantly higher than the Chinese national ambient air quality standard. The seasonal average of PM$_{2.5}$ concentration varied with the lowest concentrations of PM$_{2.5}$ in summer. Among these sites, the highest concentrations of SO$_4^{2–}$ and NH$_4^+$ ions were observed in Luoyang with the highest concentration of NO$_3^–$ detected in Zhengzhou. SO$_4^{2–}$, NO$_3^–$ and NH$_4^+$ ions occurred as (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$. For seasonal variation, the highest concentrations for Al, Fe and Ca were observed during spring in Pingdingshan and autumn in Zhengzhou and Luoyang, respectively. Enrichment factor (EF), as an indicator, is commonly used to evaluate the contribution of anthropogenic sources, and high EFs of Zn, Cu, and Cd in PM$_{2.5}$ indicate the extent of air pollution, which is generally caused by emissions of vehicles and industries. Risks posed by heavy metals on human health were assessed. The hazard index, which was used to assess the overall potential for noncarcinogenic effects, was higher than 1 in the three sites, indicating that V, Cr, As, Mn, Cd, Co, and Ni may cause accumulative noncarcinogenic health effects on humans, without the noncancer effect of each heavy metal significant. Cr in PM$_{2.5}$ is a potential carcinogenic risk when inhaled by adults. Overall, the results indicate that PM$_{2.5}$ pollution must be considered seriously in three cities.

Keywords: PM$_{2.5}$; Water-soluble inorganic ions; Secondary organic carbon; Enrichment factor; Carcinogenic risk.

INTRODUCTION

Fine particulate matter (PM$_{2.5}$) is an important atmospheric pollutant, and the sources and chemical composition of PM$_{2.5}$ are extremely complex. In addition to various sources of pollution emissions, the chemical composition of PM$_{2.5}$ contains secondary pollutants, which are formed through complex atmospheric photochemical reactions of gaseous pollutants. The main sources of anthropogenic PM$_{2.5}$ emissions are combustion, dust, and industrial emissions (Villalobos et al., 2015). Poisonous and harmful components of such particles not only deteriorate the air quality but also endanger the ecological environment. Moreover, PM$_{2.5}$ can enter the lower respiratory tract of humans, accumulate in the lungs, and access the blood stream; this behavior may cause severe harm to humans, especially children (Pui et al., 2014).

With the rapid development of economy and urbanization growth, air pollution has been a serious problem in China. At present, PM$_{2.5}$ is the primary air pollutant in large- and medium-sized cities of China. This pollutant contains water-soluble inorganic ions (WSIs), elemental carbon (EC), organic carbon (OC), and trace elements. The Ministry of Environmental Protection of the People’s Republic of China has stipulated the daily standard concentration of PM$_{2.5}$ to be 75 µg m$^{-3}$ with the annual average of 35 µg m$^{-3}$.

Many studies have investigated the physical and chemical characteristics, sources, and behavioral and formation mechanisms of PM$_{2.5}$. WSIs generally account for 40–60% of PM$_{2.5}$ composition (Pathak et al., 2009), which can provide valuable insights into the chemical characteristics of PM$_{2.5}$. Secondary inorganic aerosols (SIAs) including sulfate, nitrate, and ammonium were the major WSI components of PM$_{2.5}$. In particular, the ratio of SIAs/PM$_{2.5}$ increased during haze episodes (Wang et al., 2012). The NO$_3^–$/SO$_4^{2–}$ mass ratios varied in different regions, indicating variations...
in the energy structure and different point and nonpoint precursor NOX and SOX sources (Yang et al., 2015).

As a major component of the ambient atmospheric aerosol, carbonaceous matter can be classified into EC and OC. OC accounts for 13% to 28% of PM2.5 with small fraction of EC (3–10%) in China (Cao et al., 2007). The sources of OC are complex including the direct emission of primary organic carbon and secondary organic carbon (SOC) through physical and chemical reactions of gaseous precursors. EC is mainly produced from fossil fuel combustion and incomplete combustion of biomass (Plaza et al., 2011). Nearly 40 metal and nonmetal elements such as Mg, Al, S, P, Cl, K, Ca, Br, Ni, Cu, Fe, Mn, Zn, and Pb can also be found in PM2.5. Trace metals in PM2.5 can be used to identify the sources, although most of them constitute less than 10% of the PM2.5 (Tan et al., 2014). The enrichment factor (EF) is frequently used to identify the sources of the elements and evaluate the effects of anthropogenic factors on the concentrations of the related elements (Tan et al., 2014; Zhou et al., 2014; Hsu et al., 2016). Toxic elements, such as Pb, Cd, Ni, As, and Cr, in PM2.5 may pose potential health risks to local residents.

Henan, which is located in Central China, is one of the most populated provinces in the country. According to the CAQMA Report (2016), Henan is one of the provinces with severe PM2.5 pollution, as shown in Fig. 1 with the concentration of PM2.5 exceeding the Chinese National Ambient Air Quality Standard (NAAQS) (annual average value of 35 µg m⁻³). In the past, many actions have been taken to control PM2.5 emissions from dust, vehicles, and other major sources. Despite these initiatives, PM2.5 levels remain high. Although some studies on PM2.5 have already been conducted in Zhengzhou, the capital of Henan province, to investigate the PAHs in PM2.5, including concentrations, carcinogenic risk analysis, and source apportionment (Wang et al., 2014, 2015a), no study has focused on the chemical compositions and health risk assessment of PM2.5 in multiple cities of Henan. A one-year monitoring of PM2.5 beginning in 2014 was performed in Zhengzhou, Luoyang, and Pingdingshan, the three cities with rapid economic development in Henan. Among these cities, Zhengzhou is the most developed city in Henan. Luoyang is an important industrial base in Central China, whereas Pingdingshan is the major base in Henan for energy and raw materials, such as raw coal and crude oil.

The concentrations of WSIIs, carbonaceous species, and elements of PM2.5 were analyzed and discussed in the current study. This work investigated the seasonal variations, chemical characteristics, and possible sources of PM2.5 in Zhengzhou, Luoyang, and Pingdingshan, as well as assessed the risks posed by heavy metals (contained in PM2.5) on human health. Overall, this research provides an important technical support for regulatory agency regarding the control of air pollution in Henan, particularly the reduction of local pollutants to improve the environmental quality.

METHODS

Characteristics of the Sites

PM2.5 values were measured in the following three sites: Zhengzhou (113.32°E, 34.50°N), Luoyang (112.26°E, 34.40°N), and Pingdingshan (113.19°E, 33.43°N) (Fig. 2). Table 1 provides information related to the PM2.5 concentrations in the three cities.
Zhengzhou is located in the northern center of the province with an area of 16700 km\(^2\) and the residents population of the city is 9.38 million by the end of 2014. Given the relatively developed industry and high urbanization rate of this city, Zhengzhou was selected as a sampling area in this study. Zhengzhou experiences a subtropical wet and dry climate with an average temperature of 15.8°C (http://tongji.cnki.net/kns55/Navi/YearBook.aspx?id=N2014120113&floor=1). In 2014, the primary pollutant was PM\(_{2.5}\) and the ambient Air Quality Index (AQI) in the urban area exceeded 100 (polluted) for 202 days in 2014 (http://www.zzepb.gov.cn/Information/Content/?id=32853).

Luoyang, a famous historical and cultural city, is also an important industrial city in Henan. This city was selected for the current study primarily because of its refinery industry (processed crude oil: 64.2 Mt in 2014). PM\(_{10}\) was the main pollutant in Luoyang, and the number of days with AQI exceeding 100 (polluted) was 90 in 2014 (http://www.lyhbj.gov.cn/news/show_11124.html).

Pingdingshan is located in the middle of Henan Province. As the largest coal-producing city in Henan, Pingdingshan covers several renowned industrial regions. The total area in this city is 443 km\(^2\) by the end of 2014 (http://www.a.stats.gov.cn/hntj/lib/tjnj/2015/indexch.htm). Its climate is similar to that of Zhengzhou. PM\(_{2.5}\) was the main pollutant in Pingdingshan, and the number of days of AQI exceeding 100 (polluted) was 185 in 2014 (http://www.henan.gov.cn/zwgk/system/2015/06/05/010557331.shtml).

The Zhengzhou sampling station is located at the new campus of Zhengzhou University. This station is situated in the junction of the Lian-Huo highway on the north and the city highway in the west. The Luoyang sampling point is located in Luoyang monitoring station, which has no industry sources nearby. Sampling was performed at the roof of the fifth floor of the station (16 m). The Pingdingshan sampling site is part of the national monitoring network.

**PM\(_{2.5}\) Sample Collection**

In this research, PM\(_{2.5}\) was continuously sampled for 2 weeks during the typical months of the four seasons from summer of 2014 to spring of 2015 (n = 165) at the three sites. PM\(_{2.5}\) samples were collected on quartz microfiber filters (ALLFLEX Tissuquarts 2500QATUP, 20.32 cm × 25.4 cm) by using high-volume air samplers at flow rate of 1.13 m\(^3\) min\(^{-1}\) (TE–6070D, Tisch Environmental). The quartz microfiber filters were used to analyze the PM\(_{2.5}\) mass concentrations, WSIs, EC, and OC. In addition, Teflon filters (47 mm in diameter) using a low-volume air sampler at flow rate of 16.7 L min\(^{-1}\) (Partisol 2025i, ThermoScientific) were used to analyze elements. Aerosol sampling was conducted once a day (9:00 a.m. to 7:00 a.m. the next day). Quartz filters were precleaned at 450°C for 4 h before sampling to remove microorganic matter. The filters were placed in an environment balance with constant temperature.
and humidity (temperature: 20 ± 5°C, relative humidity: 50 ± 5%) for 48 h to constant weight in a super clean room by using a high-precision electronic balance (Mettler Toledo XS205, accuracy of 10 µg). After the sample collection, the filters were immediately placed in a super clean room to a constant weight. To prevent the loss of volatile components, the filters were placed at −18°C cold storage before analysis.

**Water-Soluble Inorganic Ions Analysis**

Water-soluble ions, comprising four anions (F–, Cl–, NO3–, and SO4 2–) and five cations (Na+, NH4+, K+, Mg2+, and Ca2+), were determined. Two pieces of circular membranes were cut from each sample filter (each piece 10.9 cm²) and then placed into 100 mL beakers. 25 mL of highly pure water was added to each beaker and then the samples were ultrasonicated in a water bath at <30°C for 30 min. The extracting solution was filtered by a hydrophilic membrane with a pore diameter of 0.22 µm before ion determination. Ion chromatographs (ICS-90, ICS-900, Dionex) were used to determine the concentrations of anions and cations. The separation column and guard column were IonPacAS11-HC4 mm and IonPacAG11-HC4 mm, respectively, for the anion determination. The eluent was composed of an 8 mM Na2CO3 and 1 mM NaHCO3 mixed solution at a flow rate of 0.8 mL min⁻¹. IonPacCS12A and IonPacCG12A were used as separation column and guard column, respectively, for the cation determination. The eluent was 20 mM methane sulfonate acid solution with the flow rate 1.0 mL min⁻¹. Standard curve was used to quantitatively analyze the samples and the R² values of standard curve for all the ions were higher than 0.999 (except for NH4+ 0.99). Each sample was measured twice, and the error was acceptable within 5%. For the recovery test, the standard addition recovery of the nine ions ranged between 89% and 110%.

**Elemental Analysis**

This study examined 27 elements: Sb, As, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, Se, Sr, Ti, Sn, Zn, Al, Ti, V, Ba, B, K, Si, and Ag. These elements were analyzed using ICP-MS (Agilent7500cx, Santa Clara, CA). A Teflon membrane filter with the collected samples was digested in a mixture of HNO3-HF-H2O2 (volume ratio 6:3:0.25) under a controlled temperature condition (30 min to heat from 20°C up to 200°C and then held for 30 min). In the experiment, a blank membrane was used to perform the blank test. For quality control of the analysis of the elements, Method detection limit was estimated using the same analysis process of the sample, and the values obtained ranged from 0.000002 µg L⁻¹ (Ag) to 0.028 µg L⁻¹ (K). The element recovery values ranged from 81% (Cd) to 110% (K). The R² values of standard curve of all the 27 trace elements were better than 0.99.

**Carbonaceous Fractions Analysis**

Two pieces of circular membrane were cut from each quartz filter and used to determine the OC and EC concentrations by using a carbon analyzer (Sunset Laboratory, US). The samples were subjected to several heating processes. The particulate OC in the sample membrane was completely released from the membrane at 580°C in a helium environment, and the EC was completely released at 870°C in a helium environment containing 2% oxygen. The instrument was calibrated by a sucrose standard solution before the experiment. Similar to the analysis of WSIs, each sample was measured twice, and the error was considered acceptable within 5%. A blank sample was measured for every 8 samples. In addition, the 10 µL sucrose standard solution (10.0000 g L⁻¹) was added to the blank filter, which was measured for every 10 samples to ensure the accuracy of the instrument. If the deviation between the measured value and the actual value (4.2 µg C µL⁻¹) was less than 5%, the instrument was accurate.

**RESULTS AND DISCUSSION**

**PM2.5 Mass Concentration**

The daily average concentrations of PM2.5 at Zhengzhou, Luoyang, and Pingdingshan sites varied in the range of 58–353, 44–315, and 27–448 µg m⁻³, respectively. As shown in Fig. 3, the annual mean concentration of PM2.5 in Zhengzhou (146 µg m⁻³) was the highest, followed by Luoyang (138 µg m⁻³) and then Pingdingshan (125 µg m⁻³). Economic development significantly influenced PM2.5 pollution. Related data such as population, GDP, and vehicle population are summarized in Table 1. Compared with the Chinese NAAQS, the PM2.5 concentrations in all monitoring sites exceeded the standard, with the annual mean values at the three sites 3.6–4.1 times higher than the standard. Thus PM2.5 pollution was extremely severe in the three sites. However, compared with the results observed in 2010 (175 µg m⁻³), 2011 (195 µg m⁻³), and 2013 (202 µg m⁻³) in same site of Zhengzhou (Geng et al., 2013; Wang et al., 2015a), the concentration of PM2.5 obtained in the current study decreased significantly. Thus previous actions taken to reduce PM2.5 pollution are apparently successful. Nonetheless the three urban sites were still with high levels of annual average PM2.5 concentration. The annual average of the PM2.5 concentrations of Pingdingshan was nearly equal to that in Wuhan (Zhang et al., 2015).

Variations in the seasonal average concentrations of PM2.5 at the three sites were observed throughout the year (Fig. 3). At the Zhengzhou site, the average concentrations of PM2.5 decreased in the order of winter (191 µg m⁻³) > autumn (143 µg m⁻³) > spring (138 µg m⁻³) > summer (110 µg m⁻³). The seasonal variation of PM2.5 concentration was the highest in winter (189 µg m⁻³) and the lowest in summer (69 µg m⁻³) at the Pingdingshan site, similar to Zhengzhou. However, the seasonal variation in Pingdingshan was more significant than that in Zhengzhou. The highest average PM2.5 concentration was observed in autumn (179 µg m⁻³) at the Luoyang site, and its average PM2.5 concentration in winter (164 µg m⁻³) was slightly lower than that in autumn.

As expected, the PM2.5 concentrations were higher in winter than those of the other seasons because of the increase in coal consumption for heating. In addition, the seasonal variation in the PM2.5 concentrations was probably affected by meteorological conditions. In winter, the meteorological conditions of the three cities were generally stable.
conditions were not conducive to the dispersion of PM$_{2.5}$ through vertical and horizontal diffusion, thus increasing the PM$_{2.5}$ concentrations. Another primary reason is the seasonal difference relative to the prevailing wind. The three cities are generally prevailing by the north winds during winter and the south winds during summer. The Beijing-Tianjin-Hebei Region is located in the north of Henan, where severe air pollution is present, causing the increase of PM$_{2.5}$ concentration due to regional transport in winter.

**Ionic Characteristics**

WSIIs, which are important components of PM$_{2.5}$, directly affect aerosol acidity, moisture, and absorption ability (Fridlind and Jacobson, 2000). Table 2 shows the seasonal average of component concentration, sulfur and nitrogen oxidation ratios (SOR and NOR), NO$_3^-$/SO$_4^{2-}$ ratio, and OC/EC ratios. The spatial distribution features of the total WSI concentrations are presented as follows: Zhengzhou (66 µg m$^{-3}$) > Luoyang (61 µg m$^{-3}$) > Pingdingshan (58 µg m$^{-3}$), and the proportions of the total WSIIs in PM$_{2.5}$ are 45%, 44%, and 46% at the three sites. Compared with the results obtained in Xi’an, which WSIIs accounted for 39.5% of the PM$_{2.5}$ mass (Zhang et al., 2011), the total WSI concentrations in the PM$_{2.5}$ of the three cities were slightly higher. In addition, NH$_4^+$, NO$_3^-$, and SO$_4^{2-}$ were the major ions in PM$_{2.5}$, which accounted for 84–91% of the total WSIIs mass. During the observation period, the trends of the NH$_4^+$, NO$_3^-$, and SO$_4^{2-}$ concentrations in PM$_{2.5}$ were consistent among the three sites in the following order: SO$_4^{2-}$ > NO$_3^-$ > NH$_4^+$. Among the sites, SO$_4^{2-}$ and NH$_4^+$ concentrations were the highest in Luoyang, and the concentration of NO$_3^-$ in the three sites follow the order: Zhengzhou > Luoyang > Pingdingshan. High concentration of SO$_4^{2-}$ is reflected by the combustion source, and high concentration of NO$_3^-$ due to both motor vehicles and power plants. Although Zhengzhou has more power plants and other stationary pollution sources than the other cities, the environmental protection measures in the former (e.g., desulfurization and denitrification measures in power plants) were implemented more effectively than those of other cities. However, a large number of vehicles, along with severe traffic jams, generate a considerable amount of NOx emissions, resulting in the highest NO$_3^-$ concentration in Zhengzhou.

The seasonal WSI concentrations are presented in Table 2. In Zhengzhou, the total concentrations of the ions were 62, 58, 55 and 90 µg m$^{-3}$ in spring, summer, autumn and winter, respectively. Similar to that of Zhengzhou, the total WSI concentration in winter was the highest in Pingdingshan (82 µg m$^{-3}$). In Luoyang, the highest concentration was...
Table 2. Seasonal average of component concentration, sulfur and nitrogen oxidation ratios (SOR and NOR), NO$_3^-$/SO$_4^{2-}$ ratio, OC/EC ratios.

<table>
<thead>
<tr>
<th></th>
<th>Zhengzhou (n = 58)</th>
<th>Luoyang (n = 52)</th>
<th>Pingdingshan (n = 55)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>autumn</td>
<td>winter</td>
<td>spring</td>
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<tr>
<td><strong>PM$_{2.5}$</strong></td>
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<tr>
<td>Gas (µg m$^{-3}$)</td>
<td></td>
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<tr>
<td>SO$_2$</td>
<td>53.0</td>
<td>90.0</td>
<td>37.4</td>
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<tr>
<td>NO$_2$</td>
<td>71.1</td>
<td>83.9</td>
<td>50.0</td>
</tr>
<tr>
<td><strong>Water-soluble inorganic ions (µg m$^{-3}$)</strong></td>
<td></td>
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<td></td>
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<tr>
<td>NO$_3^-$</td>
<td>17.9</td>
<td>26.5</td>
<td>20.3</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>19.6</td>
<td>23.5</td>
<td>19.7</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>9.2</td>
<td>19.8</td>
<td>14.4</td>
</tr>
<tr>
<td>SIA</td>
<td>46.7</td>
<td>69.8</td>
<td>54.4</td>
</tr>
<tr>
<td>WSII</td>
<td>54.8</td>
<td>90.5</td>
<td>61.6</td>
</tr>
<tr>
<td><strong>Carbon (µg m$^{-3}$)</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>OC</td>
<td>20.0</td>
<td>37.6</td>
<td>18.9</td>
</tr>
<tr>
<td>EC</td>
<td>5.2</td>
<td>17.8</td>
<td>8.1</td>
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<tr>
<td>TC</td>
<td>25.2</td>
<td>55.4</td>
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<tr>
<td>SOC</td>
<td>8.9</td>
<td>10.8</td>
<td>5.4</td>
</tr>
<tr>
<td><strong>Ratios</strong></td>
<td></td>
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<tr>
<td>OC/EC</td>
<td>3.9</td>
<td>2.1</td>
<td>2.3</td>
</tr>
<tr>
<td>SOC/OC</td>
<td>0.44</td>
<td>0.29</td>
<td>0.29</td>
</tr>
<tr>
<td>NO$_3^-$/SO$_4^{2-}$</td>
<td>0.91</td>
<td>1.13</td>
<td>1.03</td>
</tr>
<tr>
<td>WSII/PM$_{2.5}$</td>
<td>0.37</td>
<td>0.46</td>
<td>0.44</td>
</tr>
<tr>
<td>OM/PM$_{2.5}$</td>
<td>0.22</td>
<td>0.32</td>
<td>0.22</td>
</tr>
<tr>
<td>Element/PM$_{2.5}$</td>
<td>0.08</td>
<td>0.04</td>
<td>0.06</td>
</tr>
<tr>
<td>SOR</td>
<td>0.21</td>
<td>0.19</td>
<td>0.31</td>
</tr>
<tr>
<td>NOR</td>
<td>0.15</td>
<td>0.18</td>
<td>0.24</td>
</tr>
</tbody>
</table>

*The mass concentration of PM$_{2.5}$ was analyzed by Teflon filters.*
observed in autumn (75 µg m^{-3}), significantly higher than that in Zhengzhou. The SIAs and total WSII contributions to the PM_{2.5} mass values of the three sites were the highest in summer (0.48–0.56 and 0.53–0.57) because of strong atmospheric photochemical reactions. It is surprising to find that with the highest WSII concentrations observed in any particular season, both NO_{3}^- and NH_{4}^+ levels were also found to be the highest. The highest concentrations of SO_{4}^{2-} were detected in summer except for Pingdingshan (in winter). During winter, the total ion concentrations in Zhengzhou and Luoyang were similar to that in Beijing (88.8 ± 47.7 µg m^{-3}) (Yang et al., 2015), however, during spring, the total ion concentration in Beijing (83.7 ± 48.9 µg m^{-3}) (Yang et al., 2015) was higher than those in the three sites.

When NO_{3}^- and SO_{4}^{2-} exist as (NH_{4})_{2}SO_{4} and NH_{4}NO_{3}, the NH_{4}^+ concentration can be calculated as follows (Chow et al., 1996):

\[ \text{[NH}_4^+\text{]} = 0.38 \times \text{[SO}_4^{2-}\text{]} + 0.29\text{[NO}_3^-\text{]} \]  

(1)

where [NH_{4}^+] , [SO_{4}^{2-}] and [NO_{3}^-] are mass concentration in µg m^{-3}.

The actual NH_{4}^+ concentrations were larger than the results of the Eq. (1), showing that NO_{3}^- and SO_{4}^{2-} existed as (NH_{4})_{2}SO_{4} and NH_{4}NO_{3}. The main source of NO_{3}^- and SO_{4}^{2-} was fossil fuel combustion (oil and coal), and the NO_{2} and SO_{2} emissions varied in accordance with different fuel-burning processes. Thus, NO_{2} /SO_{4}^{2-} (mass concentration ratio) was used to identify motor vehicles and coal-fired sources on the atmospheric aerosol soluble relative to the contribution of each component (Arimoto et al., 1996). Compared with a stationary source, the high ratio of NO_{2} /SO_{4}^{2-} indicates the high contribution of motor vehicle emission in the atmosphere. As shown in Table 2, the average NO_{2} /SO_{4}^{2-} value in this study (0.75–0.91) was slight higher than the ratio measured in Beijing (0.71, Wang et al., 2005). In three cities, the average NO_{2} /SO_{4}^{2-} value in winter was 0.91–1.15, much higher than the value of 0.59 measured during 2001–2003 in Beijing (Wang et al., 2005), but lower than 2.2 measured in Tokyo (Saitoh et al., 2002). The major factor that drove these ratios was most likely the emissions from stationary sources, but mobile sources also may be important, and their contributions cannot be neglected. Among different sites, the highest ratios of NO_{2} /SO_{4}^{2-} were observed in autumn in Luoyang and Pingdingshan (1.38, 1.35), with the highest ratio in winter in Zhengzhou (0.91), whereas the lowest was detected in summer (Luoyang: 0.35, Pingdingshan: 0.45 and Zhengzhou: 0.59). In summer, high temperature, high RH, and high radiation are more favorable for the formation of SO_{2}^{2-}, and hypothetically the lower ratio of NO_{3}^- /SO_{4}^{2-} could be due to the higher SO_{2}^{2-} in summer. The NO_{3}^- /SO_{4}^{2-} ratios were higher than those in Chengdu (summer: 0.44 and autumn: 0.70) (Tao et al., 2013) and Fuzhou (summer: 0.17, and autumn: 0.27) (Xu et al., 2012).

SOR and NOR are often used to reflect the degree of reaction of SO_{2} into SO_{4}^{2-} and NO_{2} into NO_{3}^- in the atmosphere (Khoder, 2002). SOR and NOR were calculated as follows (Satoshi, 1986):

\[ \text{SOR} = \frac{[\text{SO}_4^{2-}]}{[\text{SO}_4^{2-}] + [\text{SO}_2]} \]  

(2)

\[ \text{NOR} = \frac{[\text{NO}_3^-]}{[\text{NO}_3^-] + [\text{NO}_2]} \]  

(3)

where [SO_{4}^{2-}], [NO_{3}^-], [SO_{2}] and [NO_{2}] are the molar concentrations.

As shown in Table 2, the annual average SOR values (0.22–0.32), especially in these three sites, showing that SO_{2} is photochemically oxidized in the atmosphere (Ohta and Okita, 1990). Without significant seasonal variation, the high NOR values (0.19–0.23) in three sites suggests that a secondary formation from NO_{2} to NO_{3}^- exists in the urban atmosphere (Lin, 2002), which were much higher than those in the Po Valley, Italy (0.04–0.05) (Squizzato et al., 2013).

**Compositions and Sources of Carbonaceous Species**

During the observation period, the total mean concentrations of OC in Zhengzhou, Luoyang, and Pingdingshan sites were 22.2 ± 14.2, 16.5 ± 10.2, and 20.5 ± 15.3 µg m^{-3} (Table 2), respectively. The organic molecule (OM = OC × 1.6) accounted for the PM_{2.5} mass concentration 24% in Zhengzhou, 19% (Luoyang), and 25% (Pingdingshan). Similar to the OC, the order of EC concentrations was Zhengzhou > Pingdingshan > Luoyang. Compared with other measurements, the annual mean OC (22.2 µg m^{-3}) and EC (9.4 µg m^{-3}) in Zhengzhou were higher than those in Dongguan (10.4 µg m^{-3}, 2.7 µg m^{-3}) (Wang et al., 2015b), but the proportions of OC in the PM_{2.5} mass in the former (15%) was lower than that in the latter (23%), with the values of EC/PM_{2.5} almost similar (approximately 7%). The annual mean EC (7.8 µg m^{-3}, 6% fine-particle contribution) in Luoyang was close to that in Beijing (7.1 µg m^{-3}, 6% fine-particle contribution) (Cao et al., 2007). The EC and OC concentrations in Pingdingshan were close to the results obtained in Chengdu (OC: 22.3 µg m^{-3}, EC: 9.0 µg m^{-3}). However, the OC and EC proportions in the PM_{2.5} mass in Pingdingshan (16% and 7%) were higher than those in Chengdu (14% and 5%) (Tao et al., 2013). It is apparent that OC and EC content within the PM_{2.5} varies with locality including different emission sources.

The seasonal variations in the carbonaceous species concentrations in Zhengzhou, Luoyang, and Pingdingshan are shown in Table 2. In Zhengzhou, the average OC and EC concentrations in winter were 3.1 and 2.6 times higher than those in summer. The average EC and OC concentrations were the highest in autumn and the lowest in summer in Luoyang. The average OC and EC concentrations in autumn were 4.5 and 3.3 times higher than those in summer in Pingdingshan. The OC and EC concentrations in summer were the lowest, mainly because the reduced pollutant emissions and prevailing wind directions in the three sites in summer were southerly, which can dilute the local
pollution. The highest OC concentrations were observed in Luoyang during autumn and in Zhengzhou and Pingdingshan during winter because of the relative importance of enhanced emission (mainly including coal consumption for heating) versus meteorology (including the subsidence of the atmospheric mixing layer, the prevailing stable atmospheric conditions, etc.) (Zheng et al., 2015). The annual OC and EC concentrations in Zhengzhou were higher than those in the two other sites, indicating that industrial emissions and mobile sources around the Zhengzhou site were more severe.

The OC/EC ratio in PM$_{2.5}$ can be used to determine the pollution source. The defined values were 1.1, 2.7, and 9.0, representing vehicle emissions, coal combustion, and biomass burning, respectively (Watson et al., 2001). In the current study, the seasonal average of OC/EC decreased in the order of autumn (3.9) > spring (2.3) > winter (2.1) > summer (1.8) in Zhengzhou. The OC/EC ratio was lower in summer, indicating that vehicle emissions played an important role in the air pollution in Zhengzhou. The seasonal average OC/EC ratios in Luoyang were 2.2, 2.0, 2.1, and 2.3, which were close to the representative OC/EC ratios of coal consumption and vehicle emissions, implying that coal burning and vehicle emissions were the main pollutant sources. In Pingdingshan, the OC/EC values were similar to those in Luoyang. Compared with the overall average OC/EC in Lanzhou (3.46) (Qiu et al., 2016), the results in the present study presented lower levels.

OC includes not only the primary organic carbon emissions by direct combustion but also the SOC by photochemical reaction. Considering the lack of direct chemical analysis method, many studies used (OC/EC)$_{\text{min}}$ to estimate the SOC concentration for simplicity (Turpin and Huntzicker, 1995; Srinivas and Sarin, 2014), which is described as follows:

$$\text{SOC} = \text{OC} - \text{EC} \times \left( \frac{\text{OC}}{\text{EC}} \right)_{\text{min}}$$  \hspace{1cm} (4)

As a result, the average SOC concentrations in the three cities varied from 5.2 to 8.1 µg m$^{-3}$, accounted for 31%-48% of OC. The SOC/OC values showed apparent seasonal variation in Zhengzhou (from 29% in spring to 44% in autumn), Luoyang (from 20% in autumn to 33% in summer), and Pingdingshan (from 20% in summer to 37% in autumn), which were lower than those detected in Wuhan (from 52.7% in spring to 58.7% in winter) (Zhang et al., 2015). The high SOC percentages were observed in Zhengzhou and Pingdingshan during autumn, whereas a high SOC percentage was observed in Luoyang during spring.

**Elements and Crustal Enrichment Factor**

Fig. 4 provides a statistical description of the seasonal concentrations of the elements associated with PM$_{2.5}$ obtained from the study area. The total element concentrations in PM$_{2.5}$ in Zhengzhou, Luoyang, and Pingdingshan were 8.5, 6.3, and 6.0 µg m$^{-3}$, which contributed about 7%, 6%, and 6% to the annual PM$_{2.5}$ mass, correspondingly. In the three sites, the most abundant trace metals in PM$_{2.5}$ were Si, Al, K, Fe, Ca, Mg, Zn, and Pb (0.15 to 3.24 µg m$^{-3}$), followed by Cr, B, Mn, Ba, Ti, Cu, Sr, Sb, Sn, and As (10 to 150 ng m$^{-3}$), and then other elements in trace amounts (0.1 to 10 ng m$^{-3}$).

The highest annual mean Si concentrations were observed in Zhengzhou (3.24 µg m$^{-3}$) and Pingdingshan (1.53 µg m$^{-3}$), which contributed 38.2% and 25.5% to the total mass of the elements in PM$_{2.5}$, respectively. However, the most abundant element in PM$_{2.5}$ was K in Luoyang (1.58 µg m$^{-3}$), and its concentration was slightly higher than that of Si (1.34 µg m$^{-3}$). The plow land area of Luoyang (432610 ha) is much larger than that of Zhengzhou (328680 ha) and Pingdingshan (321750 ha) (http://www.ha.stats.gov.cn/hnjt /lib/tjnj/2015/indexch.htm). K is attributed to biomass burning (Argyropoulos et al., 2013), and the reason for the higher K content in Luoyang may be burned more straw than other sites as indicated for larger area shown above. In the three sites, the highest average Zn and Cu concentrations were observed in Luoyang. Zn and Cu are the components of vehicle emissions (Cu is linked to brake wear, and Zn is linked to the combustion of lubricating oil) (Sternbeck et al., 2002; Han et al., 2015). Although the vehicles in Luoyang were fewer than those in Zhengzhou, the nonferrous metal production (1.4 Mt in 2014, account for 26% in Henan) (http://www.ha.stats.gov.cn/hntj/lib/tjnj/2015/indexch.htm) in Luoyang emitted a considerable amount of Cu and Zn. Compared with other Chinese cities, the average concentrations of the trace elements in PM$_{2.5}$ in Luoyang, Zhengzhou, and Pingdingshan were moderate. For instance, the average trace element concentrations in the three sites were lower than that in Taiyuan during the nonheating period (10.22 µg m$^{-3}$, which accounted for 17.3% in PM$_{2.5}$) (Liu et al., 2016).

In the three sites, the ratio of the seasonal average of the total mass element concentrations in summer (11%) was the highest, and the ratio in autumn (8%) was slightly lower in Zhengzhou than those in Luoyang and Pingdingshan. The highest ratio in summer (8%) was observed in Luoyang, and the highest ratio in spring (10.6%) was observed in Pingdingshan, probably because the three sites are located in the northern part of China, where sandstorms frequently occur in spring, and this condition leads to higher concentrations of crustal elements (Si, Al, Fe, Ca, Mg, and Ti) during spring. In addition, building demolitions and constructions significantly contribute to the high concentrations of crustal elements. For instance, the rate of urban village demolition has accelerated since 2014 in Zhengzhou, thereby increasing the concentrations of crustal elements.

EFs were calculated by dividing the relative abundance of the selected elements in the PM$_{2.5}$ samples by their average abundance in the upper continental crust (Zonta et al., 1994). The average crustal abundances were adopted from a Chinese soil background study (Wei, 1990). Al was selected as the reference element (Hsu et al., 2016). The EF was calculated as follows:

$$\text{EF} = \frac{(C/\text{Al})_{\text{PM}_{2.5}}}{(C/\text{Al})_{\text{Crust}}}$$  \hspace{1cm} (5)

where C is the element concentration.
Fig. 4. Seasonal variations of elements in PM$_{2.5}$ in Zhengzhou (a), Luoyang (b) and Pingdingshan (c).
The calculated EFs of the elements in the three sampling sites are displayed in Fig. 5. EFs are commonly used to evaluate the contribution of anthropogenic sources. Given EF > 10, the elements are mostly generated by anthropogenic sources (e.g., fossil combustion and transportation emission). When 1 < EF < 10, the elements are emitted from natural sources (e.g., soil source) and anthropogenic sources. When EF is near to 1 pointing to a crustal origin (Nolting et al., 1999). The data (Fig. 5) clearly show that the EFs of Cd, Mo, Pb, Ag, Zn, Cu, As, B, Co and Cr are higher than 10, indicating that these elements are generated by anthropogenic sources, whereas Ca, Mg, Fe, Si, and Ti achieved EFs close to unity, suggesting a soil source. The EFs of K, V, Mn, and Ba were slightly lower than 10 and higher than 1, indicating that these elements were emitted from both natural and anthropogenic sources. The EFs of Cd, Pb, Mo, Ag, and Zn were higher than 100, suggesting these elements were discharged from the industries in the three sites. For instance, the smelting and coal combustion processes emitted Pb (Zhang et al., 2009). Luoyang site presented the largest EF of Mo among the three cities due to Mo mining (the largest in China) with annual smelting capacity of 25 kt yr\(^{-1}\) (http://www.chinamoly.com/). The EFs of K and V in Luoyang and Pingdingshan sites were higher than those in Zhengzhou, indicating more severe biomass burning in Luoyang and Pingdingshan.

**Health Risk Assessment of Heavy Metals in PM\(_{2.5}\)**

People are easily exposed to heavy metals in their daily lives. The PM\(_{2.5}\) in the atmosphere enters the human body through inhalation via the mouth and nose. A health risk assessment method is generally applied to evaluate the risks caused by various pollutants, leading to noncarcinogenic and carcinogenic conditions. The carcinogenic and noncarcinogenic health risks caused by exposure to PM\(_{2.5}\) were calculated using the models from the USEPA human health risk assessment method, and exposure concentrations via inhalation were estimated to assess the health risks posed by heavy metals in PM\(_{2.5}\) by using the following equations (USEPA, 2009):

\[
EC = \frac{(C \times ET \times EF \times ED)}{AT}\]

(6)

where ET is the exposure time (6 h d\(^{-1}\)), EF is the exposure frequency (350 d yr\(^{-1}\)), ED is the exposure duration (children: 6 yr, adults: 24 yr), and AT is the average time (for noncarcinogens, AT = ED \times 365 d \times 24 h d\(^{-1}\) and for carcinogens, AT = 70 yr \times 365 d yr\(^{-1}\) \times 24 h d\(^{-1}\)). The upper bound of the 95% confidence interval (95% UCL) for the average metal concentration was used as “C” to obtain the estimate of the “reasonable maximum exposure”. The exposure risk of inhalation method then was calculated as follows:

\[
HQ = \frac{EC}{(RfC \times 1000 \mu g m^{-3})}\]

(7)

\[
HI = \sum HQ_i\]

(8)

\[
CR = IUR \times EC\]

(9)

where the hazard quotient (HQ) is the noncancer risk of a single contaminant by means of exposure. The RfC, is the inhalation reference concentration (mg m\(^{-3}\)) below which adverse noncancer health effects are unlikely to occur. If HQ < 1, the noncancer effect is believed to be not significant and may be neglected at certain times. If HQ > 1, an adverse health effect is possible, and increased attention must be given.

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**Fig. 5.** Enrichment factors for elements in three cities.
The carcinogenic risk (CR) represents the individual cancer risk caused by various chemicals. CRs exceeding $1 \times 10^{-6}$ are viewed as unacceptable. CRs below $1 \times 10^{-6}$ are not considered to pose any significant health effects. The acceptable or tolerable risk links are between $1 \times 10^{-6}$ and $1 \times 10^{-4}$, as indicated by the US EPA’s risk management.

The carcinogenic and noncarcinogenic risks from heavy metals in PM$_{2.5}$ are summarized in Table 3. For noncarcinogenic risks, among the three sites, the integrated HI values decreased in the order of Luoyang > Pingdingshan > Zhengzhou, and the HI value was higher than 1 in the three sites, indicating that these metals can cause accumulative noncarcinogenic health effects to humans. The HQ values for the seven metals (V, Cr, As, Mn, Cd, Co, and Ni) were below the safe level (HQ $< 1$), indicating that each metal exerted no significant noncarcinogenic risk effect. The HQ values yielded by Mn and Cd in the three sites were ranged from 0.25 to 0.64. In particular, the HQ value of As (0.64) in Luoyang was near the safe level (HQ = 1) and was higher than the values in Zhengzhou (0.25) and Pingdingshan (0.32). Nevertheless, Pingdingshan presented the highest HQ value of Mn (0.64) among the three sites. Compared with the results obtained in the other cities, the HQ values of As, Cd, Cr, and Ni in all studied area were considerably lower than those in Chengdu (Li et al., 2016b) but higher than those in Tianjin (Chen et al., 2015). The HQ values of Mn (0.32–0.64) in three sites were lower than that of the central area site in Baotou (0.90) (Li et al., 2016a). The HQ values of As in Luoyang were higher than those of the vehicle inspection workers in Beijing (Li, 2013). Overall, the noncarcinogenic risks induced by As and Mn must not be disregarded in Henan.

Furthermore, the carcinogenic risks to children and adults via inhalation of As, Cd, Cr, Co, Ni, and Pb were calculated. The values for As, Cd, Cr, Co, Ni, and Pb in both children and adults in the three sites were all below the acceptable level ($1 \times 10^{-4}$), indicating that the carcinogenic risk caused by these heavy metals to children and adults was acceptable. However, the carcinogenic risks of Cr to adults and children were significantly higher than the safe level ($1 \times 10^{-4}$), which were in the order of Zhengzhou > Pingdingshan > Luoyang. Given prolonged exposure, the carcinogenic risks for adults were greater than that for children in the three sites. The carcinogenic risks values for Cr, As, and Pb in children and adults were higher than those in Nanjing (Sun et al., 2014). The main emission sources of Cr are coal combustion and iron and steel production in integrated works (AEA, 2011). In addition to the carcinogenic risks causing by metals, other component present in PM$_{2.5}$ (e.g., PAHs, Dioxin and other Persistent Organic Pollutants) also exert the profound effects. Limited information in Zhengzhou indicates that the average lifetime inhaled cancer risk caused by PAHs (approximately $7 \times 10^{-7}$, Wang et al., 2014) is far less than that of metals. Thus, the government

| Table 3. Cancer and non-cancer health risk values of heavy metals in PM$_{2.5}$.
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a RfCi and IUR were cited from Regional screening level in resident air supporting tables (http://www.epa.gov/region9/superfund/prg/).

b The 95% upper confidence limit (UCL) on arithmetic mean is chosen as the exposure point concentration.
must provide necessary measures to control heavy metal emissions and protect the health of the residents.

CONCLUSIONS

A one-year observation of PM$_{2.5}$ was conducted in three monitoring sites in Henan Province to investigate the chemical characteristics of PM$_{2.5}$. The annual mean concentrations of PM$_{2.5}$ in all the sites exceeded the Chinese NAAQS, indicating that PM$_{2.5}$ pollution was extremely severe and widespread. The total WSIIs concentrations accounted for about 45% of PM$_{2.5}$. The secondary inorganic PM$_{2.5}$ ($\text{NH}_4^+$, NO$_3^-$, and SO$_4^{2-}$) was predominant WSIIs (84–91%) contributing to increased PM$_{2.5}$ concentration. NO$_3^-$, SO$_4^{2-}$, and NH$_4^+$ occurred as (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$. Coal-fired sources and vehicle were major contributors to atmospheric pollution. OC and EC were abundant component in PM$_{2.5}$ (accounted for 18–24% PM$_{2.5}$). The lowest concentrations of OC were observed in summer at all three sites, whereas the highest OC concentrations were observed in Luoyang during autumn and in Zhengzhou and Pingdingshan during winter. The secondary PM$_{2.5}$ in Zhengzhou (total of SIA and SOC is 64 µg m$^{-3}$) was more severe than those in Luoyang and Pingdingshan. The ratios of WSIIs in PM$_{2.5}$ (0.53–0.57) were the highest in summer, however OM/PM$_{2.5}$ (0.16–0.18) were the lowest in summer without significant seasonal variation. The seasonal variation of elements/PM$_{2.5}$ was obvious and the highest HI was higher than 1 in all three sites. These data can also provide insights into the similarities and differences among the urban areas in Central China. Therefore, the results may be beneficial to the development of different strategies for the improvement of air quality. One of the major tasks needs to be implemented is the establishment emission inventory so that control of the precursor gases (SO$_2$, NO$_x$ and VOCs) can be realized.

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