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 $(NH_4)_2SO_4$ and NH_4NO_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 (WSIIs), 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 $PM_{2.5}$. WSIIs 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 WSII 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

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in the energy structure and different point and nonpoint precursor NO_x and SO_x 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 $PM_{2.5}$ 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 $PM_{2.5}$. Trace metals in $PM_{2.5}$ can be used to identify the sources, although most of them constitute less than 10% of the $PM_{2.5}$ (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 $PM_{2.5}$ 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 $PM_{2.5}$ pollution, as shown in Fig. 1 with the concentration of $PM_{2.5}$ exceeding the Chinese National Ambient Air Quality Standard (NAAQS) (annual average value of 35 $\mu g\ m^{-3}$). In the past, many actions have been taken to control $PM_{2.5}$ emissions from dust, vehicles, and other major sources. Despite these initiatives, $PM_{2.5}$ levels remain high. Although some studies on $PM_{2.5}$ have already

been conducted in Zhengzhou, the capital of Henan province, to investigate the PAHs in $PM_{2.5}$, 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 $PM_{2.5}$ in multiple cities of Henan. A one-year monitoring of $PM_{2.5}$ 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 $PM_{2.5}$ were analyzed and discussed in the current study. This work investigated the seasonal variations, chemical characteristics, and possible sources of $PM_{2.5}$ in Zhengzhou, Luoyang, and Pingdingshan, as well as assessed the risks posed by heavy metals (contained in $PM_{2.5}$) 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

$PM_{2.5}$ 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 $PM_{2.5}$ concentrations in the three cities.

Fig. 1. Annual mean concentrations of $PM_{2.5}$ in cities of Henan (2014) (data from http://www.hnep.gov.cn/tabid/435/InfoID/21068/Default.aspx). The concentrations of $PM_{2.5}$ in each city were the average of $PM_{2.5}$ observed in every national monitoring site.
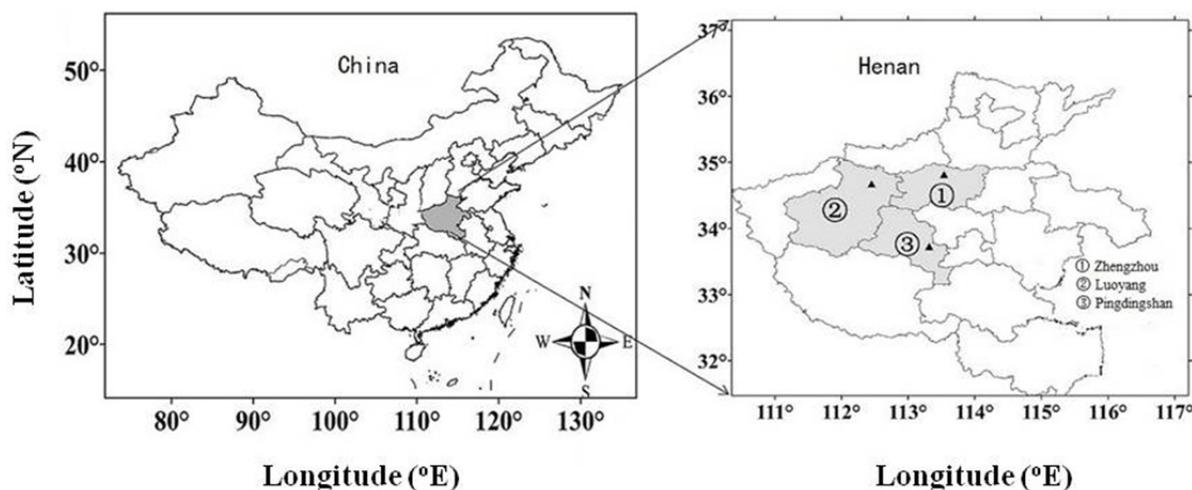
Fig. 2. Location of the sampling sites in Henan Province.

Table 1. Related information affect PM$_{2.5}$ in three cities (data from http://www.ha.stats.gov.cn/hntj/lib/tjnj/2015/indexch.htm).

City	Urban population (in million)	Developed areas (km^2)	GDP (100 million RMB[a])	Secondary industry GDP (100 million RMB)	Total energy consumption (Mt of SCE[b])	Output of electricity (100 TWh)	Vehicle population (in million)
Zhengzhou	6.4	413	6777	3487	21.23	0.50	2.22
Luoyang	3.4	194	3285	1677	15.98	0.24	0.71
Pingdingshan	2.4	73	1637	879	11.19	0.10	0.41

[a] 1 USD = 6.7 RMB.
[b] SCE = standard coal equivalent.

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, WSIIs, 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 precombusted 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: $20 \pm 5°C$, relative humidity: $50 \pm 5\%$) 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^-, NO_3^-, and SO_4^{2-}) and five cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}), were determined. Two pieces of circular membranes were cut from each sample filter (each piece 10.9 cm^2) 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 IonPacASll-HC4 mm and IonPacAGll-HC4 mm, respectively, for the anion determination. The eluent was composed of an 8 mM Na_2CO_3 and 1 mM $NaHCO_3$ 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 R^2 values of standard curve for all the ions were higher than 0.999 (except for NH_4^+ 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, Tl, 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 HNO_3-HF-H_2O_2 (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 R^2 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 WSIIs, 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

PM$_{2.5}$ Mass Concentration

The daily average concentrations of PM$_{2.5}$ 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 PM$_{2.5}$ 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 PM$_{2.5}$ pollution. Related data such as population, GDP, and vehicle population are summarized in Table 1. Compared with the Chinese NAAQS, the PM$_{2.5}$ 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 PM$_{2.5}$ 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 PM$_{2.5}$ obtained in the current study decreased significantly. Thus previous actions taken to reduce PM$_{2.5}$ pollution are apparently successful. Nonetheless the three urban sites were still with high levels of annual average PM$_{2.5}$ concentration. The annual average of the PM$_{2.5}$ concentrations of Pingdingshan was nearly equal to that in Wuhan (Zhang *et al.*, 2015).

Variations in the seasonal average concentrations of PM$_{2.5}$ at the three sites were observed throughout the year (Fig. 3). At the Zhengzhou site, the average concentrations of PM$_{2.5}$ 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 PM$_{2.5}$ 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 PM$_{2.5}$ concentration was observed in autumn (179 µg m^{-3}) at the Luoyang site, and its average PM$_{2.5}$ concentration in winter (164 µg m^{-3}) was slightly lower than that in autumn.

As expected, the PM$_{2.5}$ 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 PM$_{2.5}$ concentrations was probably affected by meteorological conditions. In winter, the meteorological conditions of the three cities were generally stable. The
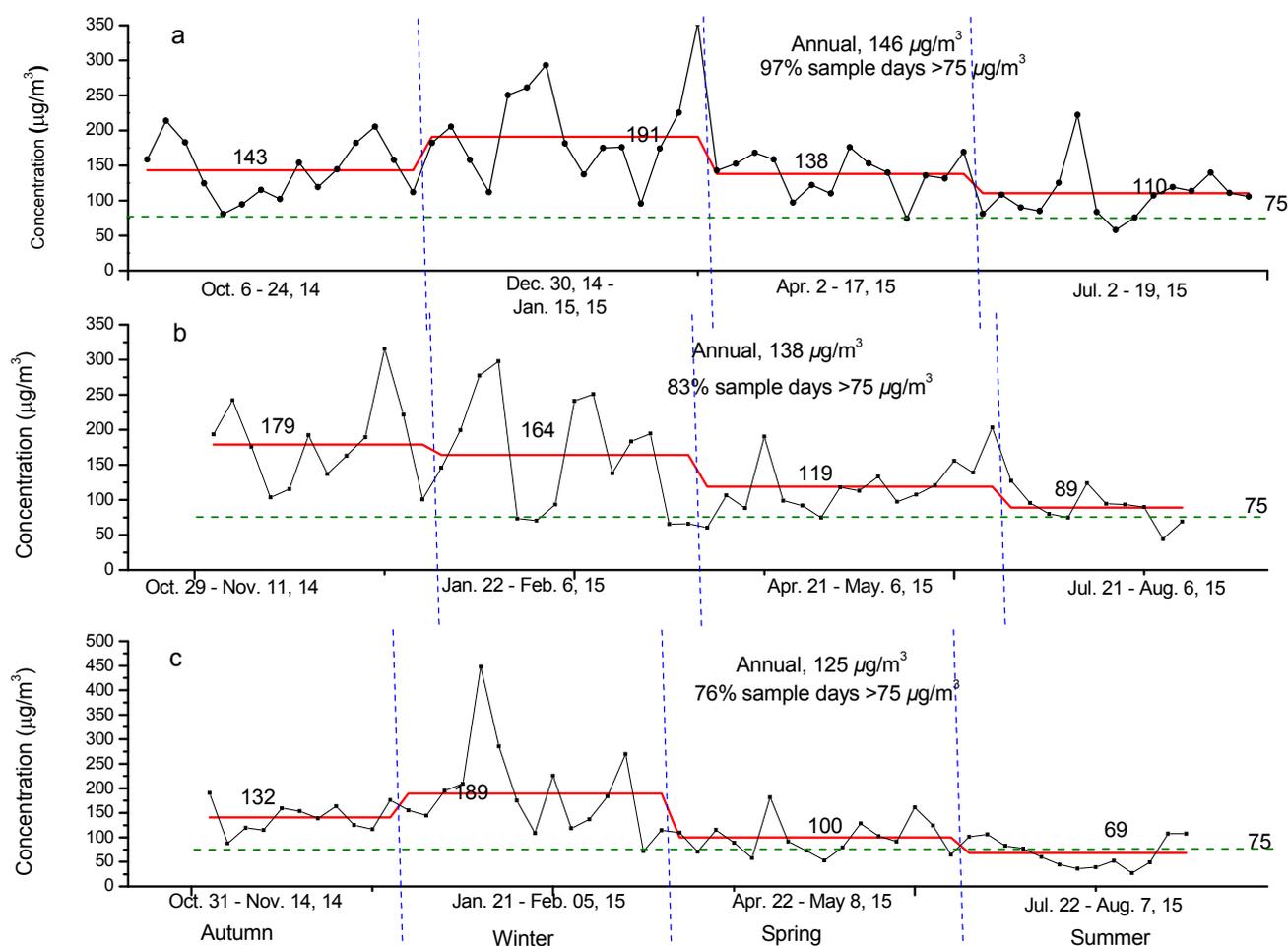
Fig. 3. Variation of PM$_{2.5}$ mass concentration during the sampling period in Zhengzhou (a), Luoyang (b) and Pingdingshan (c).

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 WSII 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 WSII 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 NO$_x$ emissions, resulting in the highest NO$_3^-$ concentration in Zhengzhou.

The seasonal WSII 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 WSII 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.

	Zhengzhou (n = 58)					Luoyang (n = 52)					Pingdingshan (n = 55)				
	autumn	winter	spring	summer	annual	autumn	winter	spring	summer	annual	autumn	winter	spring	summer	annual
$PM_{2.5}$ (µg m⁻³)	143	191	138	110	146	179	164	119	89	138	132	189	100	69	125
Gas (µg m⁻³)															
SO_2	53.0	90.0	37.4	12.3	48.6	65.8	86.1	37.5	22.9	52.4	64.5	78.1	47.3	23.2	53.7
NO_2	71.1	83.9	50.0	48.9	63.5	59.0	53.9	34.4	19.6	40.8	58.1	60.0	41.9	29.3	47.5
Water-soluble inorganic ions (µg m⁻³)															
NO_3^-	17.9	26.5	20.3	14.3	19.7	28.5	19.8	12.1	9.0	17.2	20.1	29.8	11.0	8.3	17.5
SO_4^{2-}	19.6	23.5	19.7	24.2	21.7	20.7	21.8	23.9	25.8	23.0	14.9	25.9	18.3	18.5	19.8
NH_4^+	9.2	19.8	14.4	13.9	14.2	17.7	16.5	13.4	13.8	15.3	14.2	17.2	11.1	11.7	13.6
SIA	46.7	69.8	54.4	52.4	55.9	66.9	58.0	49.5	48.6	55.5	49.2	73.0	40.4	38.5	50.8
WSII	54.8	90.5	61.6	58.3	66.1	74.8	65.5	53.0	51.3	60.9	56.5	82.3	43.9	41.0	57.5
Carbon (µg m⁻³)															
OC	20.0	37.6	18.9	12.2	22.2	27.1	18.0	12.2	9.2	16.5	32.6	29.3	15.1	6.8	20.3
EC	5.2	17.8	8.1	6.7	9.4	12.5	8.9	5.9	3.9	7.8	14.2	13.1	6.2	3.9	9.1
TC	25.2	55.4	27.0	19.0	31.5	39.6	26.9	18.1	13.1	24.3	46.7	42.4	21.4	10.7	29.4
SOC	8.9	10.8	5.4	3.9	8.1	5.4	3.8	3.6	3.0	5.2	12.2	9.9	4.1	1.4	7.6
Ratios															
OC/EC	3.9	2.1	2.3	1.8	2.4	2.2	2.0	2.1	2.3	2.1	2.3	2.2	2.4	1.8	2.2
SOC/OC	0.44	0.29	0.29	0.32	0.48	0.20	0.21	0.30	0.33	0.31	0.37	0.34	0.27	0.20	0.38
NO_3^-/SO_4^{2-}	0.91	1.13	1.03	0.59	0.91	1.38	0.91	0.51	0.35	0.75	1.35	1.15	0.60	0.45	0.88
$WSII/PM_{2.5}$	0.37	0.46	0.44	0.53	0.45	0.42	0.40	0.45	0.57	0.44	0.40	0.43	0.44	0.56	0.46
$OM/PM_{2.5}$	0.22	0.32	0.22	0.18	0.24	0.24	0.18	0.16	0.16	0.19	0.37	0.25	0.24	0.17	0.25
$Element/PM_{2.5}$ [a]	0.08	0.04	0.06	0.11	0.07	0.06	0.04	0.08	0.08	0.06	0.06	0.03	0.11	0.06	0.06
SOR	0.21	0.19	0.31	0.58	0.32	0.17	0.15	0.30	0.46	0.26	0.14	0.18	0.23	0.39	0.22
NOR	0.15	0.18	0.24	0.19	0.19	0.26	0.21	0.20	0.26	0.23	0.20	0.25	0.17	0.15	0.20

[a] 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):

$$[NH_4^+] = 0.38 \times [SO_4^{2-}] + 0.29[NO_3^-] \qquad (1)$$

where [NH$_4^+$], [SO$_4^{2-}$] and [NO$_3^-$] are mass concentration in µg m^{-3}

The actual NH$_4^+$ concentrations were larger higher 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$_3^-$/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$_3^-$/SO$_4^{2-}$ indicates the high contribution of motor vehicle emission in the atmosphere. As shown in Table 2, the annual average NO$_3^-$/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$_3^-$/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$_3^-$/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$_4^{2-}$, and hypothetically the lower ratio of NO$_3^-$/SO$_4^{2-}$ could be due to the higher SO$_4^{2-}$ 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$_x$ into NO$_3^-$ in the atmosphere (Khoder, 2002). SOR and NOR were calculated as follows (Satoshi, 1986):

$$SOR = \frac{\left[SO_4^{2-}\right]}{\left[SO_4^{2-}\right] + \left[SO_2\right]} \qquad (2)$$

$$NOR = \frac{\left[NO_3^-\right]}{\left[NO_3^-\right] + \left[NO_2\right]} \qquad (3)$$

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 summer (0.39–0.58), were higher than 0.1 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 Pindingshan (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)$_{min}$ to estimate the SOC concentration for simplicity (Turpin and Huntzicker, 1995; Srinivas and Sarin, 2014), which is described as follows:

$$SOC = OC - EC \times \left(\frac{OC}{EC} \right)_{min} \qquad (4)$$

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/hntj /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 Taian 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:

$$EF = \frac{(C/Al)_{PM_{2.5}}}{(C/Al)_{Crust}} \qquad (5)$$

where C is the element concentration.
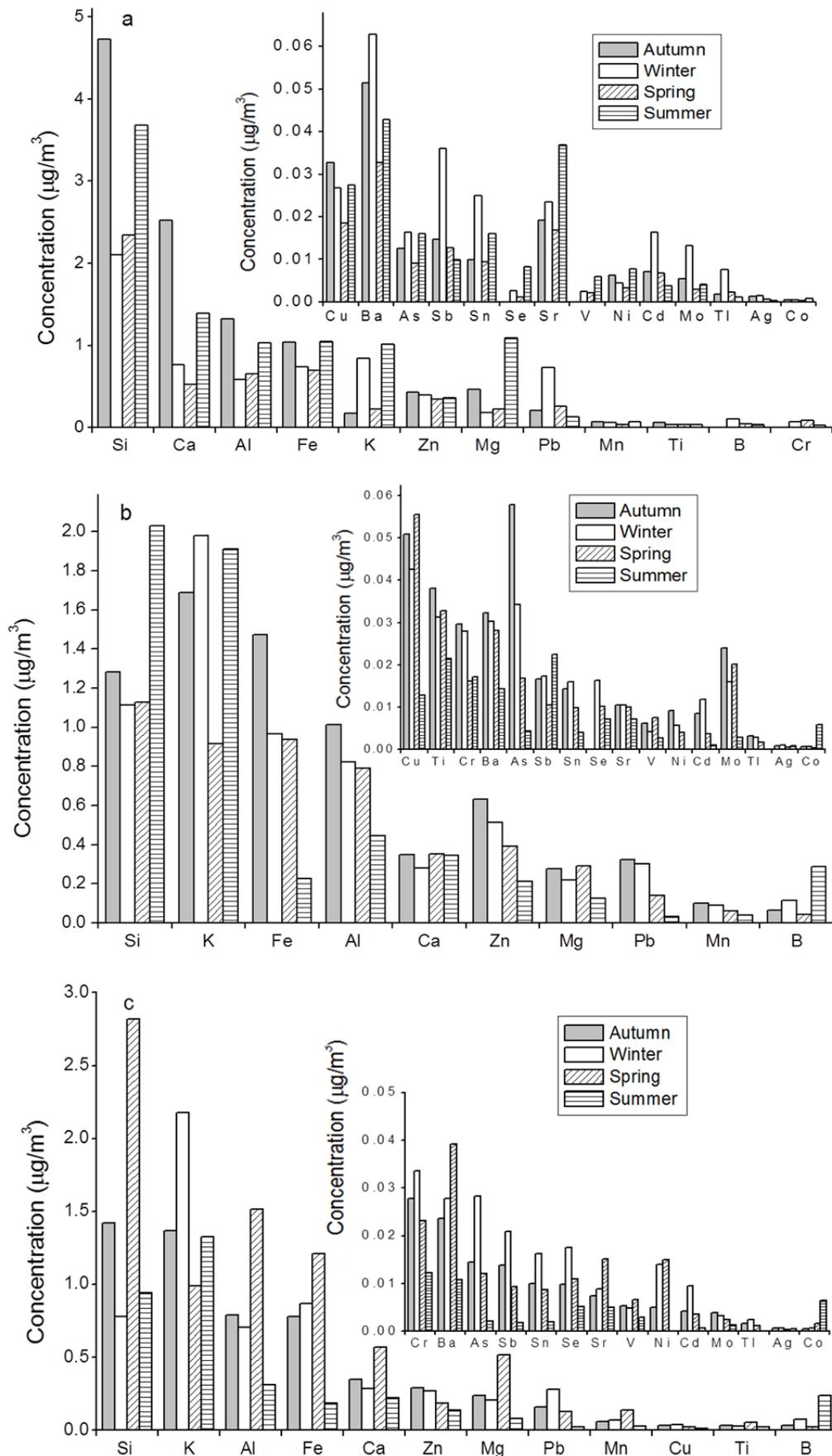
Fig. 4. Seasonal variations of elements in PM$_{2.5}$ in Zhengzhou (a), Luoyang (b) and Pingdingshan (c).

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):

$$EC = \frac{\left(C \times ET \times EF \times ED\right)}{AT} \tag{6}$$

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 × 365 d × 24 h d^{-1} and for carcinogens, AT = 70 yr × 365 d yr^{-1} × 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:

$$HQ = \frac{EC}{\left(RfC_i \times 1000 \ \mu g \ m^{-3}\right)} \tag{7}$$

$$HI = \sum HQ_i \tag{8}$$

$$CR = IUR \times EC \tag{9}$$

where the hazard quotient (HQ) is the noncancer risk of a single contaminant by means of exposure. The RfC_i 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
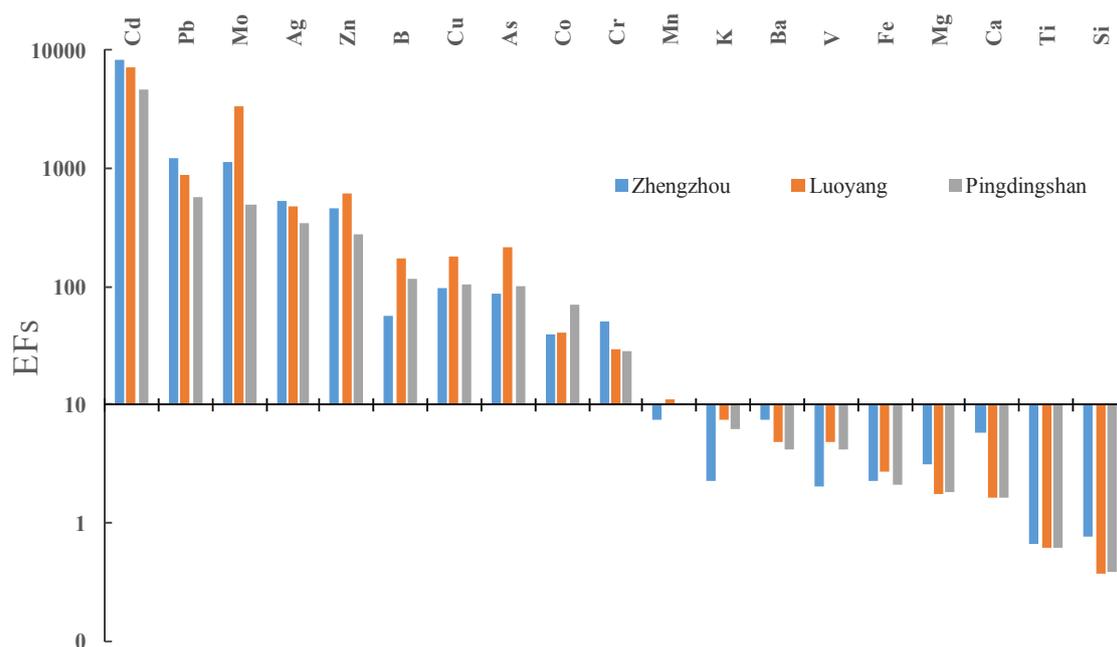

Fig. 5. Enrichment factors for elements in three cities.

(USEPA, 2009). IUR is the inhalation unit risk (m^3 μg^{-1}). The RfC_i and IUR values of the heavy metals are listed in Table 3. The hazard index (HI) is equal to the sum of the HQ of each heavy metal and is used to assess the overall potential of noncarcinogenic effects posed by various chemicals. The carcinogenic risk (CR) represents the individual cancer number among a certain number of people. CRs exceeding 1×10^{-4} are viewed as unacceptable. CRs below 1×10^{-6} are not considered to pose any significant health effects. The acceptable or tolerable risk links are between 1×10^{-6} and 1×10^{-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 (1×10^{-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 (1×10^{-6}), 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 causing by PAHs (approximately 7×10^{-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 $PM_{2.5}$.

Noncarcinogenic risk:

	RfC_i[a] (mg m⁻³)	Zhengzhou[b] (n = 58) 95%UCL (ng m⁻³)	ECinh child	ECinh adult	Noncarcinogenic risk Child-Inh	Adult-Inh	Luoyang (n = 52) 95%UCL (ng m⁻³)	ECinh child	ECinh adult	Noncarcinogenic risk Child-Inh	Adult-Inh	Pingdingshan (n = 55) 95%UCL (ng m⁻³)	ECinh child	ECinh adult	Noncarcinogenic risk Child-Inh	Adult-Inh
V	1.00E-04	4.2	1.02E-03	1.02E-03	1.02E-02	1.02E-02	6.32	1.52E-03	1.52E-03	1.52E-02	1.52E-02	5.96	1.43E-03	1.43E-03	1.43E-02	1.43E-02
Cr	1.00E-04	56.9	1.36E-02	1.36E-02	1.36E-01	1.36E-01	26.8	6.42E-03	6.42E-03	6.42E-02	6.42E-02	34.3	8.21E-03	8.21E-03	8.21E-02	8.21E-02
Co	6.00E-06	0.7	1.60E-04	1.60E-04	2.66E-02	2.66E-02	2.43	5.81E-04	5.81E-04	9.69E-02	9.69E-02	3.37	8.07E-04	8.07E-04	1.35E-01	1.35E-01
As	1.50E-05	15.5	3.71E-03	3.71E-03	2.47E-01	2.47E-01	40.0	9.59E-03	9.59E-03	6.39E-01	6.39E-01	20.3	4.86E-03	4.86E-03	3.24E-01	3.24E-01
Mn	5.00E-05	65.8	1.58E-02	1.58E-02	3.16E-01	3.16E-01	88.9	2.13E-02	2.13E-02	4.26E-01	4.26E-01	134	3.22E-02	3.22E-02	6.44E-01	6.44E-01
Cd	1.00E-05	10.3	2.46E-03	2.46E-03	2.46E-01	2.46E-01	8.61	2.06E-03	2.06E-03	2.06E-01	2.06E-01	6.29	1.51E-03	1.51E-03	1.51E-01	1.51E-01
Ni	5.00E-05	6.54	1.57E-03	1.57E-03	3.14E-02	3.14E-02	7.46	1.79E-03	1.79E-03	3.58E-02	3.58E-02	20.0	4.79E-03	4.79E-03	9.57E-02	9.57E-02
HI					1.01E+00	1.01E+00				1.48E+00	1.48E+00				1.45E+00	1.45E+00

Carcinogenic risk:

	IUR[a] (µg m⁻³)⁻¹	Zhengzhou 95%UCL (ng m⁻³)	ECinh child	ECinh adult	Carcinogenic risk (CR) Child-Inh	Adult-Inh	Luoyang 95%UCL (ng m⁻³)	ECinh child	ECinh adult	Carcinogenic risk Child-Inh	Adult-Inh	Pingdingshan 95%UCL (ng m⁻³)	ECinh child	ECinh adult	Carcinogenic risk Child-Inh	Adult-Inh
Cr	1.20E-02	56.9	1.17E-03	4.68E-03	1.40E-05	**5.61E-05**	26.8	5.51E-04	2.20E-03	6.61E-06	**2.64E-05**	34.3	7.04E-04	2.82E-03	8.45E-06	**3.38E-05**
Co	9.00E-03	0.67	1.37E-05	5.48E-05	1.23E-07	4.93E-07	2.43	4.98E-05	1.99E-04	4.49E-07	1.79E-06	3.37	6.92E-05	2.77E-04	6.23E-07	2.49E-06
As	4.30E-03	15.5	3.18E-04	5.87E-03	1.37E-06	**2.52E-05**	40.0	8.22E-04	3.29E-03	3.53E-06	**1.41E-05**	20.3	4.16E-04	1.67E-03	1.79E-06	7.16E-06
Cd	1.80E-03	10.3	2.11E-04	8.43E-04	3.79E-07	1.52E-06	8.61	1.77E-04	7.08E-04	3.19E-07	1.27E-06	6.29	1.29E-04	5.17E-04	2.33E-07	9.31E-07
Pb	8.00E-05	405	8.32E-03	3.33E-02	6.66E-07	2.66E-06	258	5.30E-03	2.12E-02	4.24E-07	1.70E-06	199	4.08E-03	1.63E-02	3.27E-07	1.31E-06
Ni	2.40E-04	6.5	1.34E-04	5.38E-04	3.23E-08	1.29E-07	7.46	1.53E-04	6.13E-04	3.68E-08	1.47E-07	20.0	4.10E-04	1.64E-03	9.84E-08	3.94E-07

[a] RfC_i 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 $PM_{2.5}$ (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 $(NH_4)_2SO_4$ and NH_4NO_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 values (0.11, 0.09, 0.11) were 3.3, 2.5, 2.3 times higher than the lowest values (0.04, 0.04, 0.04) in Zhengzhou, Luoyang and Pingdingshan, respectively. Emission control strategies aimed at mitigating $PM_{2.5}$ pollution must address the emission reduction of secondary aerosol precursors, such as SO_2, NO_x and volatile organic compounds (VOCs). EF analysis results showed that Cd, Pb, Ag, and Mo were highly enriched. Luoyang presented the largest EF of Mo among the three cities due to Mo mining. Although the noncarcinogenic risks associated with individual heavy metals were below the safe level, the overall HI was higher than 1 in all three sites, indicating that these metals can cause accumulative noncarcinogenic health effects to humans. As for carcinogenic risk to adults, the heavy metal Cr in $PM_{2.5}$ presents a significantly potential risk. Thus, the government must provide necessary measures to control heavy metal emissions and protect the health of local residents.

Consequently, the data on $PM_{2.5}$ concentration and composition in Henan can facilitate the understanding of the extent of air pollution in 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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