Distribution and Source of Chemical Elements in Size-Resolved Particles in Zhengzhou, China: Effects of Regional Transport

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ABSTRACT

To investigate the characteristics of elements in size-segregated atmospheric particulates, samples were collected using a 14-stage electrical low-pressure impactor (ELPI+) at an urban site in Zhengzhou from October 1 till 25, 2016, and analyzed for 25 elements. Results show that crustal elements were concentrated in coarse particles and toxic elements were concentrated in ultra-fine particles. The size distributions of Na, Mg, Al, Si, Ca, Fe, Ti, S and Cl were uni-modal with dominant peaks in the size range of 1.43–2.14 µm or 0.295–0.487 µm. K, P, Mn and Ba exhibited bimodal distributions, and the remaining elements showed multimodal distributions. Enrichment factor, correlation and principal component analyses indicated that vehicles were the dominant source of particles. Biomass burning, coal combustion and dust also contributed to the accumulation of particles. The elemental concentrations affected by different air masses are discussed to investigate the effects of regional transport. An increase in elemental concentrations related to vehicle and coal sources was observed when air masses came from eastern areas. Furthermore, air masses from the southeast could be a major factor in air pollution for Zhengzhou during special times, such as periods of biomass burning or naked cropland. When air masses came from the northwest, the majority of elements from dust and coal combustion were lower in concentration compared with clean days, while elements originating from vehicle emissions increased.

Keywords: Particle; Element; Size distribution; Principal component analysis; Regional transport.

INTRODUCTION

In response to the rapid economic growth, population expansion and sharp increase in motor vehicle numbers in recent years, particulate pollution has elicited increasing attention in China (Wang et al., 2016a; Wang and Chen, 2016; Gao et al., 2017), because of its detrimental effects on human health (Yang et al., 2013; Mohammed et al., 2016). Previous studies indicate that the deposition efficiencies in different parts of the human body are closely related to particle size; specifically, fine particles can penetrate deeper into the respiratory system and cause greater risk to human health (Degrendele et al., 2014; Lyu et al., 2015). As the major component of particulate matter (PM), chemical elements, such as metallic elements, are the main factors of concern. For instance, As, Cr, Ni, Zn, Cu and Cd are possibly carcinogenic, while Pb may cause fetal abnormalities (Hu et al., 2012; Cao et al., 2014; Zhou et al., 2014).

Generally, PM originates from both natural and anthropogenic sources (Villalobos et al., 2015; Landis et al., 2017). Particles larger than 1 µm are mainly generated by mechanical processes (e.g., dust resuspension, sea salt). Whereas, chemical reactions with high temperature or high enthalpy (e.g., fuel combustion, vehicle exhaust) mainly emit particles in the size range of smaller than 1 µm (Toscano et al., 2011; Masiol et al., 2015). Studies on mass size distributions can provide evidence for identifying emission sources of air pollution (Wang et al., 2016b). Moreover, size distributions of elements in size-fractionated particles can help to solve the collinearity problem in source appointment (Tan et al., 2015). For example, Cl in coarse particles primarily originates from sea salt (Masiol et al., 2015), however, combustion process, such as biomass, coal and waste burning, is the dominant source of Cl in smaller particle (Park et al., 2013; Kumar et al., 2015; Sui et al., 2016). Compared to the crustal origin of coarse particle, Ca, K and Fe detected in fine and ultrafine particles are possibly vaporized from lubricating oil (Hays et al., 2011).

During the regional transport process, dry and wet deposition, chemical reaction of particle formation can impact on the size distribution of atmospheric PM (Mateu et al., 1996; Maring et al., 2003; Mori et al., 2003). With the above considerations, elements are selected as indicators for transfer process because of their high stability (Pan et
and many studies of regional transport were carried out using elements as tracer. Pan et al. (2013) investigated the effects of long-range transport of regional emissions on the metallic concentration in downwind rural atmospheres. Zhang et al. (2012) discussed the contributions of potassium concentrations when air masses move through forest fire regions. Masiol et al. (2015) reported that atmospheric circulation has significant effects on elements concentration and size distribution. Unfortunately, these aforementioned studies only evaluated the effect of regional transport on element concentration.

In recent years, Henan province and its surrounding provinces in the central China faced with severe air pollution with high concentration of PM$_{2.5}$. The observed data indicate that the annual averages of PM$_{2.5}$ of its surrounding provinces were higher in the north (i.e., Hebei province, 77.3 µg m$^{-3}$) and east (i.e., Shandong province, 66.4 µg m$^{-3}$, Jiangsu province, 56.6 µg m$^{-3}$) than in the south (i.e., Hubei province, 65.9 µg m$^{-3}$) and west (i.e., Shaanxi province, 52.0 µg m$^{-3}$), respectively (MEP 2015). Consequently, air masses from different provinces have remarkable influences on the air quality of Henan province, resulting in that the border of many haze pollution episodes was observed in Zhengzhou, which is the capital of Henan province (Tao et al., 2012, 2014). Meanwhile, Zhengzhou is suffering from serious air pollution, registering an annual PM$_{2.5}$ average of 96 µg m$^{-3}$ in 2015 (MEP 2015). In the last few years, studies in Zhengzhou mainly focused on the chemical composition (elements, PAHs, elemental/organic carbon and water soluble ions) and source apportionment of PM$_{2.5}$ (Geng et al., 2013a, b; Wang et al., 2014, 2015). The emission sources of element and effects of regional transport on the element sources in size-resolved particles have yet to be demonstrated.

In this study, an experiment was designed at an urban site in Zhengzhou to investigate the size distribution and source of elements. Samples of size fractionated particles were collected using a 14-stage electrical low pressure impactor (ELPI+) and analyzed for 25 elements. Subsequently, enrichment factor (EF), correlation analysis (CA) and principal component analysis (PCA) based on size-segregated data were used to identify potential sources of elements. Additionally, the elemental concentrations affected by different air masses and wind data were discussed to estimate the contributions of regional transport on the source of elements in size-resolved particles.

**MATERIALS AND METHOD**

**Sampling and Analysis**

Measurements were performed from October 1 to 25, 2016, using a 14-stage ELPI+ (Dekati, Finland) with nominal cut-offs for the aerodynamic particle sizes in µm: 0.0064–0.013, 0.0134–0.021, 0.0214–0.034, 0.0344–0.056, 0.0564–0.092, 0.0924–0.176, 0.1764–0.295, 0.2954–0.487, 0.4874–0.847, 0.8474–1.43, 1.434–2.14, 2.144–3.57, 3.574–5.97, 5.974–8.86 (flux of 10 L min$^{-1}$). Additional information about ELPI+ can be found in Järvinen et al. (2014) and Yu et al. (2016). A PM$_{10}$ cyclone was used to remove large particles. The instrument is an effective tool for size-segregated particle analysis, including water-soluble ions and elements (Duan et al., 2014; Tan et al., 2015).

The sampler was installed on the rooftop (20 m above ground) of a six-story building in Zhengzhou University (34°48′N; 113°31′E), located on the northwest of Zhengzhou (Fig. 1). Details of the sampling site can be found in Geng et al. (2013a). Briefly, the sampling site is surrounded by roads and is 3 km south of the Lian-Huo Freeway and 7 km east of a belt freeway. Furthermore, a coal-fired power plant is 6 km to the east and a gas-fired power plant is 3 km to the south.

Sampling duration lasted for 24 h and polycarbonate filters (Whatman, 25 mm diameter, 0.2 µm pore size) were replaced daily at 9:00 a.m. During the study period, instruments were paused for cleaning and blank filters were installed for 24 h in the turn-off state on October 5 and 12. The samples from October 6, 14, 15, 16, 20, 21, 23 and 25 were discarded because of rainfall. In total, 210 individual sub-samples and two field blanks (total of 28) were obtained from 15 daily samples. Both samples and blank filters were stored at −20°C before analysis.

In general, there are several elemental measurements methods of aerosol samples, including X-ray fluorescence.

![Fig. 1. Location of the sampling site.](image-url)
spectrometry (XRF), Atomic absorption spectrometry (AAS), Inductively coupled plasma mass spectrometry (ICP-MS), etc. Compared with other methods, XRF is a non-destructive analytical technique with fast detection speed and high stability. While, AAS does not fit into determining multi-element sample, ICP-MS cannot yet detect non-metal elements, and both of them will take a long time in preliminary treatment (Chow and Watson, 1994). Hence, the concentrations of 25 elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Sr, Cd, Sb, Ba and Pb) of particle samples in this study were determined using an S8 TIGER Wavelength Dispersive X-Ray Fluorescence (WD-XRF) spectrometer (Bruker, Germany). WD-XRF, which utilizes crystal diffraction for observation of fluorescent X-ray, has been widely applied to element determination (Demir et al., 2008; Sarkar et al., 2010). In addition, this method has been approved by US EPA (Chow and Watson, 1994), and an official standard method named as Ambient air - Determination of inorganic elements in ambient particle matter Wavelength dispersive X-ray fluorescence spectroscopy (WD-XRF) was also issued in China. This spectrometer comes equipped with an X-ray tube with close coupling between the tube, sample and detector, which ensure a high efficiency with optimal excitation of the elements in the sample. The compact goniometer was equipped for this application with two collimators (0.23° and 0.46°), three analyzer crystals (XS-55, PET and LiF200) and two detectors (flow counter and scintillation counter) for different elements, and the voltage and current for each element were adjusted automatically by controlling the X-ray generator. Before analysis, various high quality self prepared standards were used for instrument calibration. Detail operation steps of calibration were performed referring to the published methods (Chow and Watson, 1994; Ivošević et al., 2014). Briefly, calibration coefficients were calculated using the 22 single-element MicroMatter standard filters, as listed in Table S1, by regressing the concentration data with the measured intensity data for each element. Then, the analysis software estimated the limits of detection (DLs, µg cm–2) for each calibration standards by calculating three times standard deviations of the background intensity and converting the intensity to a concentration. Moreover, the international reference material SRM 2783 supplied by the National Institute of Standards and Technology were determined and the uncertainty of relative errors (δᵣₑ) % were calculated. Overall, the range of DLs was between 0.002 µg cm–2 (Mg) to 0.034 µg cm–2 (Cd) and the δᵣₑ range from 0.1% (S) to 58.3% (Fe). Details about DLs and δᵣₑ are summarized in Table S1. Besides, four glass monitor standards were tested regularly for quick instrument check with reduced programme for Na, Al, Si, Cl, K, Ca, Sr and Sb. Meanwhile, blank filters were routinely analyzed with each batch of samples to detect sample contamination and provide quality assurance of the elemental concentrations.

**Weather Data and Back-Trajectory Analyses**

Hourly information of meteorological parameters, including temperature (T), relative humidity (RH), wind speed (WS), wind direction (WD), precipitation and air quality parameters (i.e., PM₁₀, PM₂.₅) were monitored simultaneously on the rooftop by a YG automatic weather station Model QXZ 1.0 (Yigu Technologies, China) and two tapered element oscillating microbalances (TEOM 1405, Thermo Fisher Scientific), respectively. Air mass backward trajectories were calculated daily by Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Web version model (24 h backward, starting at 9:00 am, starting a new trajectory every 6 h, at 500 m above ground level) (http://www.arl.noaa.gov/HYSPLIT.php) of the National Oceanic and Atmospheric Administration Air Resources Laboratory (Stein et al., 2015).

**Methods of Source Identification**

**Enrichment Factor (EF)**

EF is widely used to identify the origins of elements and evaluate the extent of anthropogenic influences (Granier et al., 2011). It is defined by the following formula (Chen et al., 1991):

$$EF = \left( \frac{E}{R} \right)_{\text{Air}} \left/ \left( \frac{E}{R} \right)_{\text{Crust}} \right.$$

where, E represents the investigated element, R is the reference element of crustal material, (E/R)Air is the concentration ratio of E to R in each aerosol sample and (E/R)Crust is the concentration ratio of E to R in the crust.

No widely accepted rule exists for the choice of the reference element. However, Fe, Si, Ti and Al are typically used as reference elements. In this study, Ti was selected as the reference element because it is barely affected by human activities (Chen et al., 2010).

**Correlation Coefficients and Principal Component Analysis**

As the most common standard to detect a linear relationship (Robin et al., 2013), Pearson’s CA was used to calculate the correlation coefficients (r) of elements in different modes. Furthermore, based on the principle that variables with similar characteristics can be rearranged into the same factors (Ny and Lee, 2011), PCA (Varimax Rotation) was used to identify the potential sources of those elements in this study. The Pearson’s CA and PCA were accomplished using software package SPSS version 21.0.

**RESULTS AND DISCUSSIONS**

An overview of temporal variations in the meteorological conditions and particulate mass concentrations is presented in Fig. 2. Ambient T, RH and WS during the period with effective samples were ranged from 10°C to 24°C, 53% to 88%, and 0 to 4 m s⁻¹, with average values of 17°C, 70%, and 1.1 m s⁻¹, respectively. Note that the meteorological parameters, especially the hygroscopicity properties of particles, determine the ambient particle size at water vapour subsaturation and cloud condensation nuclei (Rissler et al., 2006; Asmi et al., 2009). However, corresponding to RH data, the data of aerosol particle diameter at high time
resolution cannot be obtained by the bulk samples. Hence, the effects of meteorological conditions were not included temporary in this study during the discussion of size distribution of elements. The hourly real-time concentration of PM$_{2.5}$ peaked on October 2 (169 µg m$^{-3}$) and reached its minimum on October 22 (5 µg m$^{-3}$), with the average concentration of 47.5 µg m$^{-3}$. Three days were marked by daily average PM$_{2.5}$ values exceeded the second grade (75 µg m$^{-3}$) of the National Ambient Air Quality Standard (NAAQS) (GB 3095-2012). Meanwhile, nine days below the first grade (35 µg m$^{-3}$) were observed, which were attributed to the precipitation.

Characteristics of Chemical Elements

Elemental Concentrations

The average concentrations of 25 elements in 14 size-fractionated particles are summarized in Table S2. Data with values below the DLs were substituted by DLs/2. Given that no 50% cut-off diameters of 0.1, 1.0, 2.5 and 10 µm are in the sampler, ultra-fine, sub-micrometer, fine and coarse particle are defined as the size ranges of 0.006–0.092 µm, 0.092–0.847 µm, 0.847–2.14 µm and 2.14–8.86 µm, respectively. As shown in Table 1, most elements were accumulated in sub-micrometer and fine particles. The total concentration of analyzed elements in sub-micrometer particles was 4.6 µg m$^{-3}$, slightly higher than that in fine particles (3.9 µg m$^{-3}$), but 2.1 times in coarse particles (2.2 µg m$^{-3}$) and 6.6 times in ultra-fine particles (0.66 µg m$^{-3}$). In general, the percentage of crustal element (e.g., Na, Mg, Al, Si, K, Ca, Ti, Fe) concentration to all elements was in the order of coarse (89%) > fine (84%) > sub-micrometer (48%) > ultra-fine (39%) particles. By contrast, the order of the proportions of toxic elements (e.g., Cd, Cr, Ni, Mn, As, V, Pb), which are set a guideline by World Health Organization (WHO), was as follows: ultra-fine (9%) > sub-micrometer (4%) > coarse (2%) > fine (1%) particles. The finding indicated that compared to the fine and coarse particles dominated by crustal elements, the ultra-fine and sub-micrometer particles had a higher proportion of toxic elements, thereby possibly causing adverse health effects (Pan et al., 2013). In addition, the average concentration of Cd was 62.6 ± 78.9 ng m$^{-3}$, which exceeds the reported average level in China (13.2 ng m$^{-3}$) (Duan and Tan., 2013) by more than 4.8 times. The average concentration of As was 20.4 ± 23.7 ng m$^{-3}$, which falls below the average level in China (51.0 ng m$^{-3}$). However, both these levels are much higher than the limits prescribed in the NAAQS guidelines (5 ng m$^{-3}$ and 6 ng m$^{-3}$ in total suspended particles) and WHO guidelines (5 ng m$^{-3}$ and 6.6 ng m$^{-3}$). While the average concentrations of Ni and Pb were 7.6 ± 8 ng m$^{-3}$ and 95.1 ± 54 ng m$^{-3}$ are lower than the reported average level in China (29 ng m$^{-3}$ and 261 ng m$^{-3}$), the NAAQS guidelines (no data for Ni and 500 ng m$^{-3}$ for Pb in total suspended particles) and WHO guidelines (25 ng m$^{-3}$ and 500 ng m$^{-3}$), respectively. Even so, air pollution in Zhengzhou could pose a high risk to human health.

To recognize the status of elemental concentrations in particles in Zhengzhou, elemental concentrations from earlier studies in different cities in China and historical data at this site in 2010 are listed in Table 2. The particles smaller 2.14 µm were considered as PM$_{2.5}$ in this study. As summarized in Table 2, except for Hong Kong, the average concentrations of crustal elements such as Mg, Al, Si, K and Ca in our samples are significantly lower than those in other cities, only Ca exhibits slightly higher concentration than that in Guangzhou. Such a result indicated that during...
study periods, crustal source had fewer effects on the elemental concentration in Zhengzhou than in other cities in China. However, granted the exception, the concentrations of pollution elements such as V, Cu, Se and Cd are higher than those values observed at other cities (Table 2). In particular, Cd is considerably higher in Zhengzhou, e.g., roughly 20 times higher than that in Shanghai, 10–15 times higher than those in Beijing, Wuhan and Nanjing, and 2–5 times higher than those in Guangzhou, Xinxiang and Xi'an. It suggested that anthropogenic activity had a significant influence on pollution elemental concentration. Compared with the data at this site detected in 2010, the concentrations of Al and Ca increased significantly, which may occur because of the impact of construction activities (Pan et al., 2013). After all, urban areas in Zhengzhou have expended from 342.7 km² to 437.6 km² over the past five years (BSZ, 2010 and 2015). Additionally, the increase of vehicle quantity from 1.5 million to 2.2 million (BSZ, 2010, 2015). On the contrary, concentrations of Cr, Mn, Zn, As, Se and Pb decreased slightly, which may be attributed to the effective mitigation options on major emission sources.

**Table 1.** Mass concentration of elements in four particle modes in Zhengzhou (ng m⁻³).

<table>
<thead>
<tr>
<th>Element</th>
<th>Ultra-fine (0.006–0.092 μm)</th>
<th>Sub-micrometer (0.092–0.847 μm)</th>
<th>Fine (0.847–2.14 μm)</th>
<th>Coarse (2.14–8.86 μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean ± SD EF</td>
<td>Mean ± SD EF</td>
<td>Mean ± SD EF</td>
<td>Mean ± SD EF</td>
</tr>
<tr>
<td>Na</td>
<td>5.7 ± 3.9 0.3</td>
<td>38.1 ± 20.1* 0.8</td>
<td>33.7 ± 14.4 0.4</td>
<td>12.0 ± 5.9 0.2</td>
</tr>
<tr>
<td>Mg</td>
<td>1.8 ± 2.9 0.1</td>
<td>36.5 ± 23.9 1.0</td>
<td>112.1 ± 48.7* 1.6</td>
<td>59.9 ± 31.1 1.2</td>
</tr>
<tr>
<td>Al</td>
<td>8.8 ± 6.2 0.1</td>
<td>227.2 ± 96.6 0.7</td>
<td>413.0 ± 187.8* 0.7</td>
<td>207.7 ± 109.1 0.5</td>
</tr>
<tr>
<td>Si</td>
<td>28.2 ± 17.3 0.0</td>
<td>381.9 ± 205.4 0.3</td>
<td>609.8 ± 334.1* 0.2</td>
<td>384.6 ± 220.9 0.2</td>
</tr>
<tr>
<td>P</td>
<td>3.0 ± 2.3 3.4</td>
<td>17.1 ± 13.3* 9.2</td>
<td>8.9 ± 6.8 2.4</td>
<td>4.3 ± 4.1 1.6</td>
</tr>
<tr>
<td>S</td>
<td>180.6 ± 74.3 560.1</td>
<td>1660.1 ± 751.9* 2383.0</td>
<td>403.5 ± 222.9 296.0</td>
<td>60.7 ± 28.9 61.9</td>
</tr>
<tr>
<td>Cl</td>
<td>57.5 ± 59.0 393.7</td>
<td>270.2 ± 275.9* 855.4</td>
<td>54.5 ± 57.6 88.2</td>
<td>28.5 ± 28.9 64.1</td>
</tr>
<tr>
<td>K</td>
<td>61.9 ± 28.7 1.5</td>
<td>562.3 ± 237.4* 6.4</td>
<td>182.0 ± 90.2 1.1</td>
<td>91.1 ± 50.8 0.7</td>
</tr>
<tr>
<td>Ca</td>
<td>74.0 ± 75.4 2.2</td>
<td>409.9 ± 296.2 5.7</td>
<td>1418.5 ± 1003.7* 10.1</td>
<td>953.5 ± 565.1 9.5</td>
</tr>
<tr>
<td>Ti</td>
<td>8.2 ± 13.8 1.0</td>
<td>17.7 ± 10.5 1.0</td>
<td>34.5 ± 23.9* 1.0</td>
<td>24.8 ± 24.8 1.0</td>
</tr>
<tr>
<td>V</td>
<td>8.0 ± 7.0 45.6</td>
<td>8.0 ± 5.8 20.9</td>
<td>6.9 ± 15.0 9.2</td>
<td>10.8 ± 16.7* 20.1</td>
</tr>
<tr>
<td>Cr</td>
<td>6.8 ± 6.1* 52.1</td>
<td>6.3 ± 6.0 22.2</td>
<td>5.1 ± 4.7 9.2</td>
<td>4.7 ± 4.4 11.7</td>
</tr>
<tr>
<td>Mn</td>
<td>2.8 ± 0.0 2.3</td>
<td>45.5 ± 23.8* 16.8</td>
<td>9.3 ± 6.3 1.8</td>
<td>2.4 ± 1.5 0.6</td>
</tr>
<tr>
<td>Fe</td>
<td>70.6 ± 46.1 1.1</td>
<td>528.2 ± 193.2* 3.8</td>
<td>465.3 ± 229.4 1.7</td>
<td>206.3 ± 107.2 1.1</td>
</tr>
<tr>
<td>Ni</td>
<td>3.5 ± 5.0 60.1</td>
<td>2.1 ± 2.4 17.1</td>
<td>2.0 ± 3.5 8.3</td>
<td>12.7 ± 21.5* 72.4</td>
</tr>
<tr>
<td>Cu</td>
<td>21.9 ± 26.3 443.8</td>
<td>33.8 ± 25.4* 316.5</td>
<td>15.5 ± 16.0 74.0</td>
<td>20.4 ± 42.7 135.7</td>
</tr>
<tr>
<td>Zn</td>
<td>36.9 ± 37.3 231.7</td>
<td>174.6 ± 85.0* 508.0</td>
<td>60.5 ± 45.5 90.0</td>
<td>41.6 ± 74.1 86.0</td>
</tr>
<tr>
<td>Ga</td>
<td>6.7 ± 7.9 173.1</td>
<td>13.0 ± 9.1* 155.0</td>
<td>6.7 ± 9.8 40.7</td>
<td>9.6 ± 17.5 81.2</td>
</tr>
<tr>
<td>As</td>
<td>7.5 ± 10.6 361.5</td>
<td>10.9 ± 15.0* 243.3</td>
<td>2.1 ± 2.3 24.5</td>
<td>4.1 ± 9.3 65.5</td>
</tr>
<tr>
<td>Se</td>
<td>2.0 ± 1.6 3177.7</td>
<td>4.8 ± 4.4* 3579.7</td>
<td>1.8 ± 1.5 663.6</td>
<td>1.6 ± 1.5 832.1</td>
</tr>
<tr>
<td>Sr</td>
<td>11.8 ± 19.0* 33.1</td>
<td>7.3 ± 5.0 9.5</td>
<td>6.4 ± 4.5 4.2</td>
<td>4.8 ± 4.4 4.4</td>
</tr>
<tr>
<td>Cd</td>
<td>22.8 ± 21.2 10932.2</td>
<td>24.4 ± 32.1* 54119.0</td>
<td>15.5 ± 30.2 17551.3</td>
<td>9.3 ± 6.8 14652.7</td>
</tr>
<tr>
<td>Sb</td>
<td>6.3 ± 6.0 2435.0</td>
<td>11.7 ± 10.9* 2100.9</td>
<td>5.8 ± 4.4 532.2</td>
<td>6.1 ± 4.4 782.0</td>
</tr>
<tr>
<td>Ba</td>
<td>14.9 ± 16.0 14.8</td>
<td>19.4 ± 15.2 8.9</td>
<td>21.3 ± 25.5* 5.0</td>
<td>15.2 ± 12.1 4.9</td>
</tr>
<tr>
<td>Pb</td>
<td>10.2 ± 7.2 175.7</td>
<td>72.0 ± 39.5* 574.4</td>
<td>12.9 ± 13.4 52.6</td>
<td>4.9 ± 3.9 27.9</td>
</tr>
</tbody>
</table>

*Highest concentrations in four particle modes. Data with values below the DLs were substituted by DLs/2.

**Size Distribution**

Several studies have indicated that similar distributions of elements may come from the same source or formation mechanism (Wang et al., 2006; Masiol et al., 2015). Fig. 3 describes the size distribution of individual elements. Results show that the uni-modal distribution was observed in Na, Mg, Al, Si, Ca, Fe, Ti, S and Cl with dominant peaks in the size range of 1.43–2.14 μm or 0.295–0.487 μm, suggesting that these elements were primarily derived from single sources. K and P indicated bimodal distributions with obvious peaks in 1.43–2.14 μm and 0.295–0.487 μm. It revealed that K and P may originate from the same sources with the former elements. Na and Cl were usually used as sea-salt tracers. However, the distribution of Cl was different from that of Na in this region. Given that Cl from marine sources is more concentrated in coarse particles, Cl may come from non-sea-salt origins in Zhengzhou. Considering the similar distributions between S and K, Cl may originate from combustion processes, such as biomass burning (Sui et al., 2016). Mn and Ba also exhibited bimodal distributions, and the remaining elements had multimodal distributions with peaks in all modes, thereby signifying that those elements possibly originated from multiple sources.

Overall, elements in size-resolved particles were attributed to different origins in Zhengzhou. In the following sections, potential sources were identified comprehensively by EF, PCA and CA.

**Source Identification**

**EF Analysis**

The EF values of elements in each fraction are presented.
Table 2. Mass concentration of elements in particles and comparison with historical data and other cities in China (ng m⁻³).

<table>
<thead>
<tr>
<th>Element</th>
<th>This study</th>
<th>2010s</th>
<th>Beijing†</th>
<th>Shanghai‡</th>
<th>Guangzhou§</th>
<th>Hong Kong**</th>
<th>Xinxiang††</th>
<th>Wuhan‡‡</th>
<th>Nanjing§§</th>
<th>Lanzhou***</th>
<th>Xi’an†††</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PM₂.₅</td>
<td>PM₁₀</td>
<td>PM₂₀</td>
<td>PM₂.₅</td>
<td>PM₁₀</td>
<td>PM₂₀</td>
<td>PM₂.₅</td>
<td>PM₁₀</td>
<td>PM₀.₅</td>
<td>PM₂₀</td>
<td>PM₀.₅</td>
</tr>
<tr>
<td>Na</td>
<td>77.4 ± 39.7</td>
<td>89.4 ± 41.1</td>
<td>119.1</td>
<td>1058.6</td>
<td>1470.6</td>
<td>7105</td>
<td>7047</td>
<td>1196</td>
<td>450.0</td>
<td>1220</td>
<td>830</td>
</tr>
<tr>
<td>Mg</td>
<td>150.3 ± 74.0</td>
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<td>208.7</td>
<td>677.6</td>
<td>1908.4</td>
<td>2323</td>
<td>3378</td>
<td>314</td>
<td>830</td>
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<td>Al</td>
<td>649.0 ± 312.5</td>
<td>856.6 ± 378.3</td>
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<td>3475.5</td>
<td>2905</td>
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<td>5913.5</td>
<td>350.0</td>
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<td>2244.2 ± 1045.9</td>
<td>2304.9 ± 925.5</td>
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<td>2304.9 ± 925.5</td>
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<td>Cr</td>
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<td>Mn</td>
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<td>Ba</td>
<td>55.7 ± 45.1</td>
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<td>27.8</td>
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<td>Pb</td>
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<td>304</td>
<td>15.0</td>
<td>120</td>
<td>158.4</td>
</tr>
</tbody>
</table>

* Elemental concentration of PM₂.₅ collected at this site in 2010s (Geng et al., 2013).
† PM₂.₅ and PM₁₀ collected at Tsinghua university, Beijing, 4th–27th Dec, 2006 (Tan et al., 2015).
‡ PM₂.₅ and PM₁₀ collected at Baoshan, Shanghai, July 2009 to September 2010 (Wang et al., 2013).
§ PM₂.₅ collected at Guangzhou, 2 August to 10 September, 2004 (Wang et al., 2006).
** PM₂.₅ collected at Tap Mun, Hong Kong, 2002–2003 (Hagler et al., 2007).
†† PM₂.₅ collected at Henan Normal University, Xinxiang, 11 February to 6 March, 2015 (Feng et al., 2016).
‡‡ PM₂.₅ collected at Wuhan University, Wuhan, August 2012 to July 2013 (Zhang et al., 2015).
§§ PM₂.₅ collected at Xuanlin, Nanjing, 2013 (Li et al., 2016).
*** PM₂.₅ collected at Xigu, Lanzhou, 22nd–28th, October (Wang et al., 2016).
††† PM₂.₅ collected at Chinese Academy of Sciences, Xi’an, 1st January to 28th February 2010 (Xu et al., 2016).
in Table 1. In general, EF can be classified into three levels: (1) slight enrichment (EFs < 10), (2) medium enrichment (10 < EFs < 100), and (3) high enrichment (EFs > 100) (Wang et al., 2006). In this study, except for Mn, Sr and Ba medium enriched in sub-micrometer or ultra-fine particles, Na, Mg, Al, Si, P, K, Ca, Mn, Fe, Sr and Ba were slightly enriched, suggesting that they predominantly originated from crustal sources. In addition, V, Cr and Ni in fine mode were slightly enriched, but medium enriched in other modes, implying that both natural and anthropogenic sources may influence the emissions. The remaining elements were highly enriched in some or all modes, indicating the contributions from human activities, especially for Se, Cd and Sb. Among the four modes, the highest EF values of anthropogenic pollutant elements consistently appeared in ultra-fine mode (i.e., V, Cr, Cu, Ga, As, Cd and Sb) or sub-micrometer mode (i.e., S, Cl, Zn, Se and Pb).

CA and PCA Analysis

PCA and Pearson’s CA were performed to further identify the possible pollution sources of ultra-fine, sub-micrometer, fine and coarse particles comprehensively. Totally, there are 7, 6, 6 and 6 factors was identified and they explained a total variance of 86%, 88%, 91% and 84% for ultra-fine, sub-micrometer, fine and coarse particles, respectively. Results of varimax rotated principal component loadings for the size fractionated particles and Pearson’s correlations between each element in the four modes are listed in Tables S3 and S4, respectively. To identify the dominate sources of particles in Zhengzhou, three or four factors were selected based on the criteria of that the first three factors in each particle mode or the variance of factor is higher than 10%. Combining the factor loadings and correlation coefficients presented in Table 3 and Fig. 4, the origins of elements can be divided into the following four sources:

(1) Vehicle-Related Source

This component accounted for 30%, 38%, 34% and 36% of the total variance in ultra-fine (F1), sub-micrometer (F1), fine (F2, F3) and coarse (F1) particles, respectively. This source is identified by the highest loading for trace elements, such as Ni, Pb, Zn and V, which are commonly related to oil combustion (Lin et al., 2015; Kumar et al., 2016). Fe, Ba, Cd, Cr, Ga, Mn, Cu, As and Sb are linked to wear debris of brake linings and tire wear (Al-Khashman, 2007; Tanner et al., 2008). Hence, it was identified as vehicle-related source. Moreover, crustal elements (e.g., Na, Al, Si, K, Ti and Ca) were correlated highly with the above trace elements in sub-micrometer and coarse modes may associate with the resuspension of road dust. The average correlation coefficients between crustal and trace elements in coarse mode (r = 0.48) were lower than the sub-micrometer mode (r = 0.6), which may be attributed to the slightly obscured by crustal elements from soil dust in coarse particles. Furthermore, this vehicle-related source almost comprised the highest proportion of sources in four modes, except for fine particles, which was comparable to soil dust (39%). The findings indicated that vehicle emissions were the main source of air pollution in Zhengzhou and it suggested the government should pay more attentions on the control of vehicle source.

(2) Biomass Burning

Factor 2 in the ultra-fine mode accounted for 20% of the total variance with highest loading for S, P, Cl, K, Na and Ca. Generally, crustal source is an important origin of K, Ca, and Na. However, these elements exhibited small or
that biomass burning contributed 12%–17% of PM 2.5 in potential source of anthropogenic aerosol particles in Henan China (57.72 million tons, 2015), biomass burning is a 2012). Moreover, as the highest producer of grains in Zhengzhou (Geng et al., 2004). Thus, this factor could be associated with coal combustion. For PM 2.5, coal combustion contributed 30% (total of ultra-fine, sub-micrometer and fine) in this study, higher than the 23% in 2010 (Geng et al., 2013a). This outcome shows that the contribution of coal combustion has increased in Zhengzhou.

(4) Dust
Crustal elements (e.g., Mg, Al, Si, Ca, K, and Sr.)
characterized the F2 (17%), F1 (39%) and F2 (22%) in sub-micrometer particles, fine and coarse modes. The EFs of these elements were lower than 10 in the corresponding modes. Given the expansion of urban areas, construction dust is becoming a dominant particle source in Zhengzhou. Therefore this source can be interpreted as dust. Regional transport is a potential source of dust (Al-Khashman, 2004). Moreover, the dust will shift to smaller sizes because of gravitational settling which can preferentially remove larger particles during atmospheric transport (Maring et al., 2003). Hence, the sub-micrometer size of dust was likely influenced by long-range transport.

**Influences of Regional Transport**

Following the standard that daily mean PM$_{2.5}$ mass concentrations exceeded 35 µg m$^{-3}$, October 1, 2, 3, 7, 9, 10, 17, 18 and 19 were chosen as polluted day; by contrast, October 4, 8, 11 and 13 under 35 µg m$^{-3}$ were chosen as clean day. October 22 and 24 were ignored because of the remarkable interference of precipitation. To analysis the contributions of regional transport on the source of elements in size-resolved particles, the daily backward trajectories
of polluted days were calculated and classified into three groups by the path of air masses. The initial diagrams are presented in Fig. S1. Simultaneously, in Fig. 5, the wind rose plot of each group with average wind speed (AWS) and the percentage of wind calm hours (Clams, wind speed less than 1 m s\(^{-1}\)) were illustrated. October 1, 9, 17, 18 and 19 in group 1 (Fig. 5(a)) were characterized by the air trajectories coming from the eastern regions of sampling site, including the east of Henan province and the north of Anhui province, with the average wind speeds of 1 m s\(^{-1}\) in the ENE-E-ESE directions and 24.1% of wind calm hours. Notably, the central areas of Zhengzhou are on the path of these air masses. October 3 and 10 in group 2 (Fig. 5(b)) were composed of air masses from the southeast areas of Henan province, which are surrounded by large cultivated land, with the highest AWS (1.36 m s\(^{-1}\)) and the minimum Clams (17.3%) in the SSE direction. Air masses of October 2 and 7 from the northwest were merged as group 3 (Fig. 5(c)), which presented the lowest AWS (0.94 m s\(^{-1}\)) and the maximum Clams (27.1%) in the NWW direction.

Based on the categorized results, the concentrations of elements, which were high loading in different sources in four particle modes, were compared among polluted day, clean day and three groups. The initial data are listed in the Table S5. As shown in Fig. 6, the average concentrations of vehicle- and coal-related elements in polluted days were apparently higher than those in clean days in all particle modes. By contrast, the concentrations of crustal elements were comparable between polluted and clean days, and only the concentrations of Cl, originated from biomass burning, in polluted days were higher than that in clean days in the ultra-fine mode. These results indicated that vehicle exhaust and coal combustion were the dominant factors of particulate pollution in Zhengzhou during our sampling periods.

The vast majority of vehicle-related elements (e.g., Ni, Cr, Cu, Shb, Pb and Ba) were accumulated higher in group 1 than in clean day, which may be attributed to the traffic emissions from upwind regions. The growth rate of Zn, with high loading on vehicle source in all particle modes, increased with the size: 29.6% (32.1 ng m\(^{-3}\) in clean day–41.6 ng m\(^{-3}\) in group 1) in ultra-fine particles, 91.1% (117.3–224.1 ng m\(^{-3}\)) in sub-micrometer particles, 197.1% (31.5–93.6 ng m\(^{-3}\)) in fine particles and 474.3% (11.6–66.5 ng m\(^{-3}\)) in coarse particles. This phenomenon indicated that the east wind obviously contributed to the resuspension of road dust. Furthermore, the group 1 effects on the coal-related elements in all particle modes, and an outcome that may be ascribed to coal combustion in power plants located on the path of air masses. By contrast, the elements from dust and biomass burning in group 1 were lower than those in clean day.

Generally, most of vehicle-related (e.g., Cu, Shb, Cr, Cd, V and Ba) and coal combustion (S and Ba) elements presented lower concentrations in group 2 than in clean day, suggesting that elemental concentrations were less affected by vehicle exhaust and coal combustion in group 2. This experiment was implemented in the corn harvest period, where the higher concentration of K in this group was observed. Other elements, such as Cl, were much lower than those in clean day may be attributed to the influence of other source (e.g., waste burning) or the ultra-fine particles that evolved by complex processes in atmosphere, such as condensation, aging and deposition (Guo et al., 2012; Kumar et al., 2015). High wind speed, naked cropland after harvest and construction activities in southeast regions favored the resuspension of dust, especially for Ca. Although the average concentrations of K and Ca in group 2 were lower than those in clean day, it can become a major factor of air pollution in Zhengzhou during special periods, such as biomass burning or temporal naked cropland, when air mass came from southeast regions.

As regards to the air mass paths of polluted days in group 3, there are the Yellow River Nature Reserve and Mt. Taihang, which might lead particles to be intercepted and detained (Beckett et al., 1998). Thus, the average concentrations of crustal elements (Ca, Sr and Mn) and coal-related elements (Se and Ba) in group 3 were much lower than those in clean day. However, S from coal combustion and Cl from biomass burning were higher than those in clean day, which could be explained by the influence of transport from industrial areas of north Henan province on October 7. Higher concentrations of V, Ph, Zn and As were likewise observed, which may be ascribed to vehicle emissions on the highways that are located on the north and west of the sampling site. In addition to the effects by air masses, the weather conditions with low wind speed were conductive to the accumulation of vehicle-related elements.

In summary, air mass and wind data can be demonstrated as prominent factors of particulate pollution in Zhengzhou, requiring the government to implement joint prevention and control policy to improve air quality. Furthermore, secondary aerosol is a major source of particles in Zhengzhou (Wang et al., 2015), which cannot be clarified in this study and will thus be the focus in further research.

**CONCLUSIONS**

The characteristics and sources of 25 elements in size-resolved particles were investigated at an urban site in Zhengzhou from October 1 till 25, 2016. On average, elements were more likely to accumulate in sub-micrometer and fine particles, especially toxic elements, which had higher proportions in smaller particles. Compared with other cities, crustal sources had less effect on the elemental concentrations in Zhengzhou during the study period. However, Cd was considerably higher than in all the other cities. A uni-modal distribution was observed in Na, Mg, Al, Si, Ca, Fe, Ti, S and Cl with evident peaks at 1.43–2.14 µm or 0.295–0.487 µm. Additionally, K, P, Mn and Ba had bimodal distributions, and the remaining elements had multimodal distributions.

EF analysis was used to identify potential sources of size-resolved particles. Our results showed that Na, Mg, Al, Si, P, K, Ca, Mn, Fe, Sr and Ba predominantly originated from crustal sources and the remaining elements were influenced by human activities. Size distributions of EF values revealed that elements can easily be enriched in particles smaller than 1 µm. The results of PCA and CA.
Fig. 5. Backward trajectories and wind rose plot of polluted day in three groups: a, Group 1; b, Group 2; c, Group 3.
indicated that vehicle-related emissions were the dominant source. Furthermore, biomass burning, coal combustion and dust were also contributing factors.

The effects of regional transport on the content of size-resolved particles were also analyzed via air mass and wind data in this study. Comparisons of the elemental concentrations between clean days and polluted days in four particle modes showed that increased elemental concentrations originating from vehicle sources and coal combustion were observed when air masses came from eastern areas. Air masses from the southeast could be a major factor of air pollution for Zhengzhou in special
periods, such as biomass burning or temporal naked cropland. In addition, the majority of elements from dust and coal combustion were lower than those in clean day when air masses came from the northwest, while elements originated from vehicles emissions were accumulated. Overall, these findings reveal that particulate pollution in Zhengzhou is clearly affected by regional transport.

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SUPPLEMENTARY MATERIAL

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

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