Chemical characteristics, sources apportionment, and risk assessment of PM$_{2.5}$ in different functional areas of an emerging megacity in China

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Highlights:

- The temporal distribution of PM$_{2.5}$ components in urban, industrial, scenic, traffic, and rural sites was discussed.
- The correlations between SO$_4^{2-}$/NO$_3^-$ ratio and PM$_{2.5}$ concentrations showed different characteristics in heavy pollution days.
- Secondary aerosol, traffic, and coal combustion were identified as major sources of PM$_{2.5}$ in Zhengzhou.
- As has intolerable health risks, while Pb poses intolerable non-carcinogenic risks.

Abstract

The mass concentration, chemical composition, and source apportionment of PM$_{2.5}$ in the urban, industrial, scenic, traffic, and rural sites of Zhengzhou were studied from February to December of 2016. The average annual concentration of PM$_{2.5}$ in these five sites was 119 µg/m$^3$, which was lower than the annual average between 2013 and 2015. However, PM$_{2.5}$ pollution remains serious in Zhengzhou. PM$_{2.5}$, elemental carbon (EC), organic carbon (OC), and water-soluble inorganic ions (WSIIs)—with the exception of F$^-$, Ca$^{2+}$, and Mg$^{2+}$—showed a relatively homogeneous spatial distribution in this area. Among these pollutants, WSIIs, carbonaceous species (EC and OC), and elements accounted for 47.7%, 14.4%, and 9.6% of PM$_{2.5}$ concentration in Zhengzhou, respectively. The annual OC/EC ratio...
in Zhengzhou was 8.3, which indicates the possible presence of a secondary organic carbon. Six main sources of PM$_{2.5}$ in Zhengzhou, namely, soil dust (15.1%), coal combustion (17.6%), secondary aerosol (35.1%), vehicle traffic (17.3%), industry (7.3%), and biomass burning (7.7%), were identified by using a positive matrix factorization model. The results of the back trajectory and potential source contribution function analysis revealed that the air mass from regions of the Shandong and Hubei Provinces aggravated the pollution in Zhengzhou, and Puyang, Hebi, Xinxiang, and Kaifeng were the main potential sources of PM$_{2.5}$, respectively. The carcinogenic risks of As to children through the ingestion pathway exceeded the acceptable level. The findings of this work can provide an in-depth understanding of the PM$_{2.5}$ pollution in Zhengzhou.

**Keywords:** PM$_{2.5}$; spatial distribution; positive matrix factorization; coefficients of divergence; health risk assessment

**1 Introduction**

China's economy has grown rapidly over the past decade and has propelled a rapid increase in the amount of air pollutant emissions from anthropogenic sources (Zhou et al., 2016). Atmospheric particulate matter (PM), especially PM$_{2.5}$, is a primary air pollutant that has received significant attention because of its negative effects on human health, visibility, and climate change (Pope and Dockery, 2006; Bytnerowicz et al., 2007; Mohsenibandpi et al., 2017; Jiang et al., 2019b; Li et al., 2019). The diverse effects of PM$_{2.5}$ may be ascribed to its complex chemical components, such as its water-soluble inorganic ions (WSIIIs), elements, carbonaceous substances, and organic components (Wang et al., 2009; Zhang et al., 2016; Liu et al., 2017; Jiang et al., 2018b). Fully understanding the chemical composition of PM$_{2.5}$ can help identify the sources (Jiang et al., 2018e) and effectively control this pollutant (Yang et al., 2011). Introduced by Paatero and Tapper, positive matrix factorization (PMF) is a sources allocation receptor model that is widely used for identifying the main sources of atmospheric...
pollutants in many places worldwide (Brown et al., 2015; Contini et al., 2016; Lan et al., 2016; Jiang et al., 2018d). Meanwhile, hybrid single-particle Lagrangian integrated trajectory (HYSPLIT) and potential source contribution function (PSCF) are important models for assessing the potential sources or regions of pollutants (Liu et al., 2018; Jiang et al., 2019a). Many studies have also examined the chemical characteristics and source distribution of PM$_{2.5}$ in the developed regions of China, including the Yangtze River Delta, Pearl River Delta, and Beijing–Tianjin–Hebei (Gu et al., 2011; Zhang et al., 2013; Li et al., 2016; Tan et al., 2016; Du et al., 2017; Huang et al., 2017). However, only few studies have examined the Central Plains Economic Region, where the atmospheric PM$_{2.5}$ have reached extremely serious levels (the annual average concentrations: 125-146 $\mu$g/m$^3$, Jiang et al., 2017), especially in Zhengzhou (Ministry of Environmental Protection of the People’s Republic of China, 2017). As the core city of the Central Plains Economic Region, Zhengzhou is located south of the North China Plain and in the lower reaches of the Yellow River with a population of about 10 million. Zhengzhou has a rapidly growing economy with its Gross Domestic Product (GDP) increased from RMB 498.0 billion in 2011 to RMB 811.4 billion in 2016 (ZMBS, 2017). The leading industries in this city include equipment manufacturing, automobile, electronic information, biology and medicine, new materials, modern food manufacturing, aluminum and aluminum deep processing, home manufacturing, and brand clothing. From 2011 to 2016, the number of motor vehicles in Zhengzhou increased from 1.6 million to 2.7 million (ZMBS, 2017), which subsequently increased the emission of atmospheric pollutants in the city and resulted in a severe air pollution.

To date, only few studies have produced chemical speciation data for the PM$_{2.5}$ pollutants
in Zhengzhou (Geng et al., 2013; Jiang et al., 2018c). Moreover, very few systematic studies have conducted multi-point analysis, source analysis, and health risk assessment of PM$_{2.5}$ components. Previous studies have highlighted many differences among the various sampling sites in the different functional areas of a single city. For instance, Han et al. (2015) found that the contribution of crustal elements in residential areas was higher than that in other regions, while the level of toxic metals in cement industrial areas was generally higher compared with that in other areas. A higher degree of PM$_{2.5}$ pollution is often in urban areas than in rural areas (Gao et al., 2016). Given its significant role in promoting air pollution, conducting a chemical characterization and source apportionment of PM$_{2.5}$ in the different regions of Zhengzhou is imperative. Therefore, by exploring the chemical characteristics and source apportionment of PM$_{2.5}$ in different areas of Zhengzhou, this study produces very meaningful findings and conclusions for both researchers and policymakers.

The concentration, spatial distribution, and source apportionment of PM$_{2.5}$ in the rural, urban, industrial, scenic, and traffic areas of Zhengzhou are examined in this work. The five primary objectives of this work are to (1) understand the characteristics and spatial distributions of PM$_{2.5}$ and chemical species, (2) perform source apportionment by using the PMF model, (3) ascertain the potential source regions by using the PSCF model, (4) evaluate the health risk posed by toxic elements, and (5) analyze the various characteristics of heavy pollution days.

**2 Experimental methods**

**2.1 Sampling sites**

PM$_{2.5}$ was collected in the rural, urban, industrial, scenic, and traffic sites of Zhengzhou.
from February to December of 2016 (Fig. 1). The scenic site, Dengfeng (DF), has relatively few industries located nearby and lies in the southwest suburb of Zhengzhou. As a traffic site, Hangkonggang (HKG) lies in the south suburb of the city and is located 3.6 km away from Xinzheng International Airport. Situated in the east suburb of Zhongshan, Zhongmu (ZM) is a rural site located near a large farmland area and has no obvious industrial source. Xinmi (XM), which lies in the southwest suburb of the city, acts as the important industrial site of Zhengzhou. The 47th middle school (SSQ) lies in the urban area of the city and is located near the convention center and main road. Table 1 presents detailed information about these sampling sites.

2.2 Sampling

Middle-volume sampling instruments (100 L/min; TH-150AII, Tianhong, China) were used to collect PM$_{2.5}$ samples from each site. Two sampling filter membranes were used, including polypropylene filters for analyzing the elements (90 mm in diameter; Tianjin Xinyao, China) and quartz microfiber filters for analyzing the other chemical constituents (90 mm in diameter; Tianjin Xinyao, China). PM$_{2.5}$ samples were collected from 10 a.m. on the first day to 9 a.m. on the second day. Quartz filter before sampling in a muffle furnace at 450 °C baking 5 h eliminate organic matter may affect.

The filter was placed in ultraclean room balance (20±5 °C temperature and 50±5% relative humidity) for 48 h. Afterward, high-precision electronic weighing scales (Mettler Toledo XS205) with a weight difference of no more than 0.03 mg were used to weigh the
samples twice to guarantee weighing precision. The samples were then stored in a freezer at
−20 °C before the analysis.

2.3 Chemical analysis

Half of each quartz filter sample was used to determine the concentrations of the nine
WSII ($F^-, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}$, and $Ca^{2+}$) via ion chromatography (ICS-90,
ICS-900, Dionex, USA). More details can be found in Yu et al. (2018).

A 1.45 cm$^2$ filter was intersected with a punch in a quartz fiber filter, and then OC and EC
were analyzed with a carbon analyzer (Sunset Laboratory, USA). Two temperature rise steps
were performed in the analysis. This process is described in detail in Jiang et al. (2018a).

A total of 21 metallic compounds and elements (Na, Ba, Mg, Sb, Al, Sr, Si, K, Se, Ca, Ti,
Ga, V, Ni, Pb, Cu, Zn, As, Fe, Mn, and Cr) in the filters were measured by using an S8 TIGER
wavelength dispersive X-ray fluorescence spectrometer (Bruker, Germany), which usage has
been approved by the US Environmental Protection Agency (USEPA; Chow and Watson,
1994). Additional information can be found in Wang et al. (2018).

2.4 Coefficients of divergence (CDs)

CDs, as a self-normalizing parameter, were evaluated to understand the differences and
similarities in the concentrations observed in the five sampling sites. This parameter was
computed as follows (Park and Kim, 2004; Kuo et al., 2014):
\[
CD = \sqrt{\frac{1}{m} \sum_{i=1}^{m} \left( \frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}} \right)^2 },
\]  
(1)

where $x_{ij}$ and $x_{ik}$ are the concentrations of chemical component $i$ in sites $j$ and $k$, respectively,
and $m$ is the number of measurement days. In the previous analysis (Contini et al., 2012), the
values of these coefficients can be used to infer the spatial homogeneity of PM$_{2.5}$ composition in different sites. If the CDs approach 0 or lower than 0.2, then the two sampling sites have a relatively homogeneous spatial distribution. Meanwhile, if the CDs approach 1, then these two sampling sites are different.

### 2.5 Back trajectory analysis

The 48-hour backward air trajectories in the five sampling sites with 4-hour intervals were calculated by using the HYSPLIT-4 model (US National Oceanic and Air Administration Air Resources Laboratory). The altitude was set to 500 m. Meteorological data from the Global Data Assimilation System were also used in the calculation.

### 2.6 PSCF model

The PSCF model was used to ascertain the potential source regions (Liu et al., 2018). The pollution value of PM$_{2.5}$ was 75 $\mu$g/m$^3$, the study domain ranged from 31° N to 38° N and from 102° E to 115° E, and the resolution of the grid cells was 0.3°×0.3°. Other detailed descriptions can be found in the Supplemental Materials.

### 2.7 PMF model

The PMF model, which is widely applied as a receptor model (Paatero and Tapper, 1994; Paatero, 1997), divides the sample data matrix into two (factor contribution (G) and feature profile (E)) to quantitatively identify the source of contaminants. The factor contributions and profiles were derived via the PMF model by minimizing the objective function $Q$. The identification of data matrix $X$, objective function $Q$, and uncertainty is further described in the Supplemental Materials.

In this study, the program was run several times to find the smallest value of $Q_{\text{expect}}$ and to
reduce the observed value of residual error matrix \( E \) as much as possible in order to ensure that the simulation results show a good correlation with the observations. The stability of a PMF solution was estimated based on the bootstrap (BS), displacement (DISP), and BS-DISP results. After running the program several times, the number of sources was set from four to nine, and the results of six sources were selected due to their adequate fit to the measurement data and their physical meaning (more details can be found in Table 2). These results were constrained with \( \text{dQ}_{\text{robust}} \) of 0.6%, and \( F_{\text{peak}} = 0.0 \) produced the most physically reasonable source profiles.

### 2.8 Health risk assessment

The United States Environmental Protection Agency (USEPA) developed an assessment model for estimating the carcinogenic and non-carcinogenic health risks of being exposed to particles. This study was based on the following assumptions. The target subjects were divided into two groups (Jiang et al., 2018e), namely, children < 15 years and adults. The non-carcinogenic risks from V, Cu, As, Mn, Zn, Pb, and Ni and the carcinogenic risks from As, Pb, and Ni for children and adults were calculated from three exposure pathways, including inhalation, ingestion, and dermal absorption. The exposure and risk assessments are described in Jiang et al. (2018e).

To evaluate the human health risks of these pollutants, in addition, different sources of the same element have different levels of toxicity. The results of the PMF model were combined with those of the risk assessment model. The non-carcinogenic risk index hazard quotient (HQ) and carcinogenic risk index (CR) of the pollution sources were computed as

\[
HQ \text{ or } CR = \sum_{i=1}^{n} X_i \times HQ_i \text{ or } CR_i \quad \text{...(2)}
\]
where $X_i$ denotes the contribution of each pollution source derived from the PMF model to the $i$ element in the entire sampling period, while $HQ_i$ and $CR_i$ are the $i$ element risk values calculated by the risk assessment model described above.

3 Results and discussion

3.1 PM$_{2.5}$ mass concentrations

The annual mean PM$_{2.5}$ concentration in the five sampling sites in 2016 was 119 µg/m$^3$ (Fig. 2 and Table S1), which was 2.4 times higher than the annual concentration standard (35 µg/m$^3$) proposed by the Chinese National Ambient Air Quality Standard (NAAQS). Although lower than those values in 2013 (191 µg/m$^3$), 2014 (185 µg/m$^3$), and 2015 (150 µg/m$^3$; Jiang et al., 2018c), the 119 µg/m$^3$ concentration exceeded those that were in the Yangtze River Delta (60 µg/m$^3$; Feng et al., 2015), Taiwan (24 µg/m$^3$; Hsu et al., 2017), and Lecce (Southern Italy, 19 µg/m$^3$; Cesari et al., 2017), thereby underscoring the severity of PM$_{2.5}$ pollution in Zhengzhou. The daily PM$_{2.5}$ concentration in the city varied from 18 µg/m$^3$ to 666 µg/m$^3$, over half (60.5%) of which exceeded the daily standard of the Chinese NAAQS (75 µg/m$^3$). This proportion can even reach as high as 98% during winter. Meanwhile, the seasonal average PM$_{2.5}$ concentration demonstrated the following decreasing order: 221±126 µg/m$^3$ (62 µg/m$^3$ to 666 µg/m$^3$) in winter, 98±34 µg/m$^3$ (39 µg/m$^3$ to 200 µg/m$^3$) in spring, 88±39 µg/m$^3$ (37 µg/m$^3$ to 218 µg/m$^3$) in autumn, and 47±16 µg/m$^3$ (18 µg/m$^3$ to 86 µg/m$^3$) in summer. The main factors that influence the PM$_{2.5}$ concentration included the characteristics and loads of pollution sources, particulate characteristics, and meteorological factors. The low PM$_{2.5}$ concentrations during summer can be ascribed to the initiative of the Zhengzhou Municipal Environmental Protection Bureau to reduce the amount of pollutant emissions
Meanwhile, the high PM$_{2.5}$ concentrations in winter may be ascribed to the increased amounts of emissions, such as those from coal-fired heating, and adverse meteorological conditions, such as frequent winter temperature inversion and relatively stable atmospheric conditions (Liu et al., 2017).

The PM$_{2.5}$ concentrations of the five sampling sites are presented in Table S1. The results showed that the highest annual mean PM$_{2.5}$ concentrations were observed in the urban site of SSQ (137±113 µg/m$^3$) and the traffic site of HKG (131±91 µg/m$^3$), followed by the rural site of ZM (112±112 µg/m$^3$) and the industrial site of XM (111±85 µg/m$^3$) and the lowest annual mean PM$_{2.5}$ concentration (104±82 µg/m$^3$) was in the scenic site of DF. The differences in the PM$_{2.5}$ concentrations of the five sampling sites were calculated based on CDs (Fig. 3) SSQ and HKG have the lowest CD values, possibly because they have a large amount of traveling vehicles and airplanes, thereby implying that vehicle emission may have an important role in increasing the PM$_{2.5}$ concentration. Relatively few emission sources were reported near DF, which is a scenic area. A lag time in the PM$_{2.5}$ concentration peak was also in each sampling site as shown in Fig. 2. Specifically, the concentration peak appeared earliest in ZM and latest in DF, which may be explained by the heavy pollution days transfer from the northeast.

### 3.2 Characteristics of chemical species in PM$_{2.5}$

#### 3.2.1 WSII analysis

Consistent with previous studies (Squizzato et al., 2013; Yin et al., 2014; Meng et al., 2016), this paper identified nine WSIIIs that comprise PM$_{2.5}$ (Table S1). These WSIIIs...
accounted for 47.7% of the annual PM$_{2.5}$ mass concentration and 47.9%, 42.3%, 51.2%, and 49.4% of the PM$_{2.5}$ mass concentrations in winter, spring, summer, and autumn, respectively.

Compared with other cities such as Wuhan (43.7% to 41.8%; Zhang et al., 2015) and Shanghai (32.0%; Wang et al., 2006a), Zhengzhou has a higher ratio of WSIIs/PM$_{2.5}$, thereby indicating that WSIIs are important constituents of the atmospheric PM$_{2.5}$ pollutants in the city.

The annual WSIIs concentrations in Zhengzhou demonstrate the following decreasing order: NO$_3^-$ (20.4±24.2 µg/m$^3$) > SO$_4^{2-}$ (17.7±17.6 µg/m$^3$) > NH$_4^+$ (13.2±11.4 µg/m$^3$) > Cl$^-$ (2.6±3.5 µg/m$^3$) > Ca$^{2+}$ (1.5±1.5 µg/m$^3$) > K$^+$ (1.4±2.0 µg/m$^3$) > Na$^+$ (0.4±0.3 µg/m$^3$) > F$^-$ (0.2±0.2 µg/m$^3$) > Mg$^{2+}$ (0.1±0.1 µg/m$^3$). Secondary inorganic aerosols (SIAs) (NH$_4^+$, SO$_4^{2-}$, and NO$_3^-$) were the major components of these WSIIs and accounted for an average of 88.4% of the total ions in the five sampling sites across all four seasons. This percentage is nearly the same as those reported in Beijing (86.3%, Deng et al. 2011), Handan (87.0%, Meng et al., 2016), and Hefei (82.0%, Deng et al., 2016).

The seasonal variations in the WSIIs are shown in Table S1. The seasonal concentrations of SO$_4^{2-}$ and Cl$^-$ were highest in winter, which may be related to coal-burning heating for residents in North China in this season. In addition, the stable atmospheric structure in winter is not conducive to the diffusion of pollutants. NO$_3^-$ had the highest contribution in winter due to the combined action of photochemical and heterogeneous reactions, NO$_x$ emissions, and gas–aerosol equilibrium (Zhang et al., 2013). NH$_4^+$ concentration was larger in winter because of poor dispersion and the lower removal rate in this season. However, the highest concentrations of Mg$^{2+}$ and Ca$^{2+}$ were observed in spring, which may be ascribed to the dry
winds blowing in the area during this season. By contrast, the concentration of all WSIIs were lower in summer, because the height of the planetary boundary layer is higher in summer, which is contributes to the diffusion of pollutants (Yang et al., 2015). In addition, the lowest concentration of NO$_3^-$ in summer may be related to the loss of nitrate particles to the gaseous phase due to the high temperature in summer (Diapouli et al., 2017). Meanwhile, the CD results showed that Na$^+$, K$^+$, NO$_3^-$, and SO$_4^{2-}$ followed a relatively homogeneous spatial distribution while all the other WSIIs demonstrated varying characteristics across the five sampling sites, especially in DF (Fig. 3).

The equivalent concentrations of cations (CE) and anions (AE) were computed as

$$AE = \frac{SO_4^{2-}}{48} + \frac{NO_3^-}{62} + \frac{Cl^-}{35.5} + \frac{F^-}{19} \quad \text{and} \quad (3)$$

$$CE = \frac{Na^+}{23} + \frac{NH_4^+}{18} + \frac{K^+}{39} + \frac{Mg^{2+}}{12} + \frac{Ca^{2+}}{20} \quad \text{and} \quad (4)$$

Fig. 4 presents the scatter diagram of AE versus CE in all four seasons. The samples collected in each season were above the 1:1 (CE:AE) line, thereby suggesting that the cations were not completely neutralized by anions and hence showed an alkaline property (Meng et al., 2016). This observation can also be attributed to the existence of other anions, such as CO$_3^{2-}$ and HCO$_3^-$, which were not analyzed in this study. Meanwhile, the sample collected for winter, specifically the sample with a higher concentration, was below the 1:1 (CE:AE) line and showed an acidic property, thereby suggesting that the ion composition of PM$_{2.5}$ in winter was more complex than the compositions of PM$_{2.5}$ in other seasons. This finding explains why the most serious level of air pollution is often observed during winter (Huang et al., 2016). Fig. 5 presents the scatter plots of (a) NH$_4^+$ versus SO$_4^{2-}$ and (b) NH$_4^+$ versus [SO$_4^{2-}$+...
NO₃⁻]. This figure further illustrates how NH₄⁺ relates to the major acidic ions, including 
SO₄²⁻ and NO₃⁻. Fig. 5(a) shows that SO₄²⁻ can be fairly sufficient to be neutralized by NH₄⁺; 
therefore, (NH₄)₂SO₄ is the existence form of SO₄²⁻. Fig. 5(b) shows that all samples are 
positioned around the 1:1 line, thereby indicating that the PM$_{2.5}$ samples occupy a sufficient 
NH₄⁺ to neutralize SO₄²⁻ and NO₃⁻ to (NH₄)₂SO₄ and NH₄NO₃, respectively. Given that 
(NH₄)₂SO₄ is less volatile than NH₄NO₃, the former can be formed preferentially. The results 
of a comparative analysis show that a high PM$_{2.5}$ concentration, especially above 300 µg/m$^3$, 
significantly deviates from the 1:1 line, which in turn may suggest that NH₄⁺ is not enough to 
cancel out SO₄²⁻ and NO₃⁻ simultaneously. Therefore, NO₃⁻ exists in the form of NH₄NO₃ 
and HNO₃ (Meng et al., 2016, Zhang et al., 2013).

The mass ratio of NO₃⁻/SO₄²⁻ can be used to indicate the relative contribution of fixed 
and mobile sources in the atmosphere (Xiao and Liu et al., 2004, Yao et al., 2002). According 
to Arimoto et al. (1996), a high NO₃⁻/SO₄²⁻ ratio indicates that the contribution of mobile 
sources is more significant than that of stationary sources. In this study, the average annual 
ratio of NO₃⁻/SO₄²⁻ in Zhengzhou was 1.0 (Table S2). Meanwhile, the mass ratio in the city 
was greater than the NO₃⁻/SO₄²⁻ ratio (0.63) in Heze from 2015 to 2016 (Liu et al., 2017) and 
less than the mass ratio (1.10) in Hefei from 2012 to 2013 (Deng et al., 2016). The high 
NO₃⁻/SO₄²⁻ mass ratio in Zhengzhou may be attributed to the high traffic density in the city. 
The average NO₃⁻/SO₄²⁻ mass ratio also showed seasonal variations in the following 
decreasing order: winter (1.3) = autumn (1.3) > spring (1.0) > summer (0.4). The lowest mass 
ratio of NO₃⁻/SO₄²⁻ was during summer probably because the stability of NH₄NO₃ was 
reduced under the high temperatures during summer and the rate of NO₃⁻ formation decreased.
Meanwhile, the high mass ratios of $\text{NO}_3^-/\text{SO}_4^{2-}$ in winter and autumn may be attributed to the fact that the low temperatures increased the rate of $\text{NO}_3^-$ formation (Deng et al., 2016).

### 3.2.2 Carbonaceous material analysis

The average annual concentration values of OC and EC in Zhengzhou were 15.4 and 2.1 $\mu$g/m$^3$, which accounted for 12.6% and 1.8% of PM$_{2.5}$, respectively (Table S1). This level was close to the values of carbon aerosols observed at regional sites throughout China (16.1±5.2 $\mu$g/m$^3$ for OC and 3.6±0.9 $\mu$g/m$^3$ for EC; Zhang et al., 2008).

Similar to PM$_{2.5}$, the seasonal changes of OC and EC were reduced in the following order: winter (30.8 $\mu$g/m$^3$ and 4.0 $\mu$g/m$^3$) > autumn (10.9 $\mu$g/m$^3$ and 1.6 $\mu$g/m$^3$) ≈ spring (10.8 $\mu$g/m$^3$ and 1.7 $\mu$g/m$^3$) > summer (5.8 $\mu$g/m$^3$ and 0.7 $\mu$g/m$^3$). The OC and EC concentrations in SSQ (18.2 $\mu$g/m$^3$ and 2.2 $\mu$g/m$^3$) and HKG (16.6 $\mu$g/m$^3$ and 2.7 $\mu$g/m$^3$) exceeded those in ZM (15.4 $\mu$g/m$^3$ and 2.2 $\mu$g/m$^3$), XM (13.0 $\mu$g/m$^3$ and 2.0 $\mu$g/m$^3$), and DF (13.9 $\mu$g/m$^3$ and 1.5 $\mu$g/m$^3$) mainly due to the influence of vehicle emissions. The coefficient of correlation ($R^2$) between OC and EC in autumn exceeded those in other seasons (Fig. S1), thereby suggesting that OC and EC may come from similar sources in autumn to a certain extent. In sum, OC and EC demonstrate various characteristics in different sampling sites in different seasons.

OC comprises secondary organic carbon (SOC) and primary organic carbon (POC). Previous studies (Turpin and Huntzicker, 1995; Zhang et al., 2007; Zhang et al., 2013) have demonstrated the possible existence of SOC when the OC/EC ratio exceeds 2.0 to 2.2. In this study, the average annual OC/EC ratio was 8.3, which slightly varied across seasons (9.9, 8.7, 7.6, and 7.0 in winter, summer, autumn, and spring, respectively). These variations may indicate the presence of SOC in the atmosphere (Zhang et al., 2007; Zhang et al., 2013).
contribution of SOC to the formation of secondary organic aerosols can be estimated by calculating SOC as follows (Yuan et al., 2005):

\[
SOC = OC - POC = OC - EC \times \left(\frac{OC}{EC}\right)_{\text{min}},
\]

where SOC (µg/m³) and OC (µg/m³) are the concentrations of SOC and OC, respectively, and \((OC/EC)_{\text{min}}\) represents the minimum OC/EC ratio in each site across different seasons throughout the sampling period.

In this study, SOC concentrations followed a decreasing order: winter (13.0±15.0 µg/m³) > autumn (5.1±3.9 µg/m³) > spring (4.2±3.2 µg/m³) > summer (2.2±1.7 µg/m³). The SOC/OC and SOC/PM_{2.5} ratios were obviously high during autumn, which may be explained by the contributions of various sources and the influence of meteorological conditions on the formation of SOC. SOC significantly contributed to the OC and PM_{2.5} mass in SSQ, thereby suggesting that the unique topography around the urban center was prone to the accumulation of atmospheric pollutants and the formation of SOC (Li et al., 2016).

### 3.2.3 Elements

A total of 21 elements (Zn, Na, Ca, Al, Si, K, Mg, Ni, Ti, V, Cu, As, Fe, Mn, Cr, Pb, Ga, Se, Sr, Sb, and Ba) were detected in PM_{2.5} and accounted for 9.6% of the PM_{2.5} studied in this paper (Table S3). Crustal elements (i.e., Fe, Si, K, Ti, Ca, Mn, Mg and Al) dominated the tested elements of PM_{2.5} and accounted for 93.1% of all tested elements in Zhengzhou. High crustal elements concentration was observed in spring probably because of the frequent dust weather events during this season (Genget al., 2013). The CD values for these elements are presented in Fig. 3. The pollution characteristics of DF, especially the elements from anthropogenic resources (e.g., Zn, Cr, Ba, and As) obviously differed from those of other sites.
The characteristics of crustal elements (Ca, Mg, Al, Si, and Ti) in ZM were different from those in SSQ because ZM is an agriculture area (Liu et al., 2017) whereas SSQ is an urban area (Aldabe et al., 2011). SSQ and HKG demonstrated similar pollution characteristics. In general, the differences in the chemical species analyzed in the five sampling sites were significant.

The concentrations of crustal elements in the PM$_{2.5}$ collected from the five sampling sites followed a decreasing order: SSQ (13.0±12.3 µg/m$^3$), HKG (12.9±14.2 µg/m$^3$), XM (10.1±9.0 µg/m$^3$), ZM (5.8±3.6 µg/m$^3$), and DF (5.7±5.7 µg/m$^3$) (Table S3). The high concentrations of crustal elements in HKG and SSQ might be attributed to vehicles sweeping a large amount of dust on the road, while the low concentrations in ZM and DF could be attributed to the scarcity of soil sources around these rural and scenic areas (Table 1). Although the elements (i.e., Zn, V, Sb, Cr, Sr, Ni, Se, As, Ga, Cu, Pb, and Ba) accounted for only 6.9% of the measured elements in Zhengzhou, they are all deemed toxic to humans. The annual concentrations of As in all sites, especially in SSQ (17.8±15.7 ng/m$^3$), greatly exceeded the Chinese NAAQS limit of 6 ng/m$^3$. By contrast, the average annual concentrations of V, Pb, Mn, and Ni were below the limits set by (World Health Organization) WHO (25, 500, 150, and 1000 ng/m$^3$ for Ni, Pb, Mn, and V, respectively).

The influence of human activities and the natural background of those particles associated with the elements were determined by analyzing the enrichment factor (EF) (Zheng et al., 2004; Betha et al., 2014; Jiang et al., 2017), which was calculated by using Eq. (6) (Taylor et al., 1964; Hsu et al., 2010). In the following, Al was taken as the reference element and the concentration of elements in the surface soil of China was taken as the crust elements
concentration value in the crust (Hsu et al., 2016).

\[ EF_x = \frac{(E/Al)_{\text{particulates}}}{(E/Al)_{\text{crust}}} \]  

(6)

where \((E/Al)_{\text{particulates}}\) and \((E/Al)_{\text{crust}}\) are the concentration ratios of the target metal to the reference element Al in the samples and the continental crust, respectively. In this study, an EF value of below 10 indicates that the element mainly comes from natural sources, while an EF value of above 10 indicates that the element may come from human sources (Xu et al., 2013; Zhang et al., 2015).

The EF values of each element of PM\(_{2.5}\) collected from the five sampling sites across different seasons are presented in Figs. S2-3, which show that Si, K, Mg, Mn, Ti, Fe, Cr, Ba, V, Ni, and Sr have annual average EF values of lower than 10. Therefore, these elements mainly come from crustal sources (Xu et al., 2013). Ca, Cu, As, Ga, Na, Zn, Pb, and Sb were enriched with annual average EF values of above 10, thereby suggesting that these elements are influenced by human sources (Zhang et al., 2015). Zn, Pb, and Sb (with annual average EF > 100) were anomalously enriched. Generally, many metals (i.e., Na, K, Mg, Pb, Ba, As, and Sr) showed high EF values during winter, while some metals (Mn, Cu, Cr, V, Ni, Ga, and Sb) showed high EF values during summer. Fig. S2 shows that the EF values of many metals, except for Si, Ca, Fe, Ni, and Ga, are high in ZM.

3.3 Chemical mass closure

An PM\(_{2.5}\) chemical mass closure was structured in the five sampling sites in consideration of SIAs, dust, EC, organic matter (OM), WSIIIs (\(F^-\), \(K^+\), \(Cl^-\), \(Mg^{2+}\), \(Na^+\), and \(Ca^{2+}\)), and elements, except for crustal elements (Ca, Al, Ti, Fe, and Si). In this study, OM was estimated as OC multiplied by 1.8 in Chinese cities (Tao et al., 2014, Wang et al., 2006a).
The dust was calculated by the crustal species as

\[
[Dust] = 1.94 \times [Ti] + 2.20 \times [Al] + 2.42 \times [Fe] + 1.63 \times [Ca] + 2.49 \times [Si],
\] (7)

The chemical composition that was reconstructed based on the seasonal and annual average concentrations of PM$_{2.5}$ in the five sampling sites is shown in Fig. 6 and Table S1. SIAs had the highest proportion across all five sampling sites and accounted for more than 40.0% of the annual PM$_{2.5}$ concentration in Zhengzhou, with the largest and smallest values in DF (46.3%) and SSQ (40.0%), respectively. OM showed minimal differences across all sampling sites (large in SSQ and DF (24.0%) and small in XM (19.8%), with an average of 22.7%). By contrast, dust exhibited significant differences across all sites (19.3%, 12.7%, 14.0%, 18.9%, 10.6%, and 15.1% in HKG, ZM, XM, SSQ, and DF, respectively). The ratios of EC, WSIIs, and elements (except for crustal elements) in PM$_{2.5}$ were 1.8%, 4.8%, and 0.6% on average, respectively. Obvious seasonal changes were also reported in dust (significantly larger in spring and smaller in winter and summer), OM (larger in winter and smaller in spring), SIAs (larger in summer and smaller in spring), and elements (slightly larger in summer and autumn and smaller in winter and spring).

3.4 Source apportionment by PMF

The PMF model was used to determine the contributions of sources by using the datasets collected from the five sampling sites as input data. PMF analysis was performed on 23 species, including OC, EC, Na, NH$_4^+$, SO$_4^{2-}$, NO$_3^-$, Al, Ca, V, Mg, Si, Zn, Cl, K, As, Se, Ti, Ni, Cu, Pb, Cr, Mn, and Fe, all of which were classified as “strong” variables (Jiang et al., 2018e). The data for these species satisfy the requirements for PMF 5.0 input data analysis.
Six primary sources of PM$_{2.5}$, namely, secondary aerosol, coal combustion, dust, biomass combustion, vehicular traffic, and industry, were eventually identified (Fig. 7).

The first factor was related to dust with high abundance of Na, Mn, Al, Si, Ti, Mg, Fe, and Ca in PM$_{2.5}$ than other species. Soil and road dusts are major species in the atmosphere that mainly comprise Ca, Fe, Al, Mg, K, and other elements (Lough et al., 2005; Jiang et al., 2018a). Dust has an annual contribution of 15.1% to the PM$_{2.5}$ pollution in Zhengzhou (Table 3); this percentage was lower than those in Lanzhou in 2014 (21.8%; Wang et al., 2016) and Heze between 2015 and 2016 (19.2%; Liu et al., 2017) but was higher than those in Beijing (8.6%), Tianjin (11.7%) and Shijiazhuang (8.5%) between 2014 and 2015 (Huang et al., 2017). Similar to the findings of Zhang et al. (2013) and Chen et al. (2017), the contributions of dust in the PM$_{2.5}$ pollution in Zhengzhou showed an obvious seasonal distribution. For instance, a higher dust concentration was observed in spring (21.3%±18.3%), which can be ascribed to the frequent sandstorms in Zhengzhou during this season (Jiang et al., 2018e). A significant difference was also observed across all five sampling sites. Specifically, high contributions were observed in SSQ (18.2%) and HKG (17.5%), which echoed the results for chemical mass closure.

The second factor was categorized as vehicular traffic, which is characterized by OC, EC, NO$_3^-$, V, Ni, Cu, Zn, Pb, and Mn, all of which are often considered tracers of vehicular traffic (Charlesworth et al., 2011, Viana et al., 2006). Cu is related to break wear, and Ni is produced by the combustion of oil (Garg et al., 2000). Vehicular traffic accounted for 17.3% of the
PM$_{2.5}$ mass in Zhengzhou and did not show any obvious seasonal variation probably due to
the annual uniform emission load. Compared with other cities in China, the contributions of
vehicular traffic to air pollution in Zhengzhou are relatively high, only less than Beijing
between 2014 and 2015 (24.9%; Huang et al., 2017) and Lanzhou in 2014 (21.7%; Wang et
al., 2016). An obvious difference was also observed among the five sampling sites, with SSQ
(22.1%) and HKG (18.6%) showing the largest contributions while XM (13.4%) showing the
lowest contributions. These percentages could be ascribed to the characteristics of these sites.

The third factor showed a high loading for Cl$^-$, OC, Na$^+$, SO$_4^{2-}$, As, Na, and Pb, all of
which are mainly produced by the burning of coal (Bhangare et al., 2011). This factor
accounted for 17.6% of the PM$_{2.5}$ mass in Zhengzhou; this percentage is lower than that in
Lanzhou in 2014 (22.3%; Wang et al., 2016) and Chongqing between 2012 and 2013 (22.0%;
Chen et al., 2017). The high contributions of coal combustion to the PM$_{2.5}$ pollution in
Zhengzhou during winter was closely associated with the high amounts of coal that is burned
during this season to generate heat. No obvious seasonal variations were observed in the
contributions of this source. Coal combustion showed a significant contribution to the PM$_{2.5}$
pollution in XM (20.4%) but only a small contribution to the PM$_{2.5}$ pollution in HKG
(15.9%).

The fourth factor had high loadings on SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$, so it could be identified
as the nitrates and sulfates of mixed source of secondary aerosols. The gaseous precursors
(NO$_x$, NH$_3$, and SO$_2$) generated by human activities are main sources of secondary ions that
are formed in the atmosphere (Perrone et al., 2010). A previous study showed that NO$_3^-$,
SO$_4^{2-}$, and NH$_4^+$ are primarily produced by the chemical reactions of particles (Wang et al.,
This source contribute 35.1% to the PM$_{2.5}$ concentrations in Zhengzhou. Although lower than that in Beijing between 2014 and 2015 (40.5%; Huang et al., 2017), this percentage implies a serious degree of secondary aerosol pollution in Zhengzhou. A significant seasonal variation was also observed for this source in the following decreasing order: summer (41.9%) > winter (35.0%) > autumn (33.7%) > spring (31.2%). The intense secondary aerosol reaction reported in summer and winter similar to the results findings of Zhang et al. (2013) and Chen et al. (2017). The highest contribution of secondary aerosols was reported in DF.

The fifth factor was identified as industry, which was mainly comprised As, V, Pb, Ni, Cr, Se, and Cu, all of which are generally associated with industrial processes (Chan et al., 1997; Turpin and Lim, 2001). Industry contributes around 7.3% to the PM$_{2.5}$ pollution in Zhengzhou; this percentage is obviously lower than that reported in Tianjin between 2014 and 2015 (11.7%; Huang et al., 2017), Beijing between 2009 and 2010 (25.0%; Zhang et al., 2013), and Chongqing between 2012 and 2013 (19.7%; Chen et al., 2017). However, this percentage was higher than in Beijing between 2014 and 2015 (3.2%; Huang et al., 2017) and Heze between 2015 and 2016 (3.8%, Liu et al., 2017). The influence of the environmental supervision conducted by the Zhengzhou Municipal Environmental Protection Bureau between December 18 and 20 in 2016 explains why this source showed the lowest contribution in summer (5.8%) and the largest contribution in autumn (8.1%).

The sixth factor was highly loadings on K, Cl, EC, and OC, which could be related to biomass burning (Argyropoulos et al., 2013). Biomass-burning activities, including wildfires in summer, prescribed burning in spring all the way through fall, and heating in winter, occur
all year round in Zhengzhou. Biomass combustion contributes to the PM$_{2.5}$ pollution in Zhengzhou during autumn and winter at an average annual rate of 7.7%, which is higher than that reported in Beijing between 2009 and 2010 (12.0%; Zhang et al., 2013). The highest contribution was observed in ZM (10.7%), followed by XM (7.6%) and DF (7.3%).

Compared with the results obtained in 2013 (Geng et al., 2013) where soil dust, vehicle traffic, secondary aerosol, coal combustion, industry, and mixed sources (biomass burning, oil combustion, and incineration) accounted for 26.0%, 10.0%, 24.0%, 23.0%, 4.0%, and 13.0% of the PM$_{2.5}$ pollution in Zhengzhou, respectively, this study reported lower contributions of soil dust and higher contributions of secondary aerosol, vehicle, and industry. These differences underscore some significant changes in the pollution source and emission load. Moreover, the source apportionment results pointed toward the typical characteristics of the five sampling sites. The contributions of vehicle traffic and dust were obviously higher in the urban and traffic sites, thereby indicating the serious degree of vehicle pollution in these areas. The highest contribution of industry was observed in the industrial site, while that of biomass burning was observed in the rural site. These observations were consistent with the characteristics of these areas and can support the government in their decision making.

3.5 Back trajectory analysis

The results of the backward trajectory analysis on heavily polluted days via the HYSPLIT-4 model are presented in Fig. 8. The air masses from the northeast directions caused the most serious pollution in the entire study area, except in DF. More than 1/3 of the air masses (44.4%, 61.1%, 33.3%, and 38.9% for the ZM, HKG, XM, and SSQ sites, respectively) came from Shandong Province during the heavy pollution period. The air masses originating from
Hubei Province were also dominant (27.8% to 66.7%) in these sites, especially in DF with highest value of 66.7%. The PM$_{2.5}$ concentrations were higher in SSQ (537.0 µg/m$^3$), ZM (510.1 µg/m$^3$), and HKG (410.6 µg/m$^3$) compared with the other sites, which may be explained by the accumulation of air pollutants during the long-range transport from Shandong Province and Hubei Province. In addition, XM (38.9%) and SSQ (33.3%) derived air masses from the Shaanxi Province, while some cluster (33.3%) in DF originated from the western provinces (starting from Gansu Province and passing over Shaanxi Province). The lowest PM$_{2.5}$ concentrations were observed in XM and DF (354.4 µg/m$^3$ and 362.4 µg/m$^3$, respectively), which suggest that these sites are relatively cleaner than the other examined areas.

3.6 PSCF results

Combined with the backward trajectory analysis, the spatial distribution of potential PM$_{2.5}$ source regions and transportation paths of SSQ are shown in Fig.9. The potential sources with WPSCF values of higher than 0.4 were mainly distributed northeast (Puyang, Hebi and Xinxiang) and east (Kaifeng) of SSQ. These findings indicate that the migration of atmospheric pollutants in the agricultural areas of Henan Province has a great impact on the PM$_{2.5}$ pollution in urban areas. In addition, the WPSCF value of Nanyang above 0.7, thereby suggesting that the long-distance transmission of pollution sources also contributes to the PM$_{2.5}$ pollution in SSQ.
3.7 Health risk assessment

The carcinogenic risks of toxic elements in three exposure pathways from different pollution sources in the five sampling sites are shown in Table S4-5. The health risks of As (9.7×10⁻⁵ to 2.6×10⁻⁴ for children and 4.9×10⁻⁵ to 1.3×10⁻⁴ for adults) and Pb (5.7×10⁻⁶ to 9.8×10⁻⁶ for children and 2.9×10⁻⁶ to 5.0×10⁻⁶ for adults) were mainly accumulated through intake. Ni was mainly distributed through the intake (6.7×10⁻⁵ to 1.1×10⁻⁴ for children and 3.4×10⁻⁵ to 5.6×10⁻⁵ for adults) and dermal channels (4.7×10⁻⁵ to 7.7×10⁻⁵ for children and 3.4×10⁻⁵ to 5.6×10⁻⁵ for adults). The carcinogenic risks values of all elements for children were higher than adult via intake and dermal exposure at all sites, while children were below adult via inhalation. The carcinogenic risk values of As from ZM, XM, SSQ, and HKG via ingestion for both children and adults (except for HKG) were higher than 1.0×10⁻⁴, thereby indicating a serious potential cancer risk. Meanwhile, the carcinogenic risk values of Pb and Ni from all sampling sites via inhalation were lower than 1.0×10⁻⁶, thereby implying that the carcinogenic risk can be ignored.

The non-carcinogenic risks of toxic elements (V, Cu, As, Mn, Zn, Pb, and Ni) in three exposure pathways from different pollution sources in the five sampling sites are shown in Table S6-7. The highest cumulative HQ values of As (2.7 to 7.2 for children and 3.4×10⁻¹ to 9.1×10⁻¹ for adults) and Pb (2.4 to 4.1 for children and 3.0×10⁻¹ to 5.2×10⁻¹ for adults) were mainly distributed in the intake pathway. Meanwhile, the HQ values of V, Cu, Mn, Zn, and Ni via the three exposure pathways were all below the safety level of HQ = 1, thereby suggesting that their potential non-carcinogenic risk could be ignored. The HQ values of As and Pb for children via ingestion were above the safety level of HQ = 1, thereby indicating the serious
non-carcinogenic risks of these elements.

The HI\textsubscript{ing} (ingestion) values of the toxic elements in the five sampling sites ranged from 6.0 (DF) to 12.1 (ZM) for children and from 0.8 (DF) to 1.5 (ZM) for adults. These values exceed the safety level (except for the HI\textsubscript{ing} value in DF). Meanwhile, the HI\textsubscript{der} (dermal) values of these elements ranged from 0.8 (DF) to 1.3 (ZM) for children, which were above the safety level (except for the HI\textsubscript{der} value in DF), thereby suggesting that the potential non-carcinogenic risk of these elements warrants further attention. The HI\textsubscript{inh} (inhalation) values were below the safety level in all five sampling sites, thereby indicating that the non-carcinogenic risk of these elements can be ignored.

Each element in the five sampling sites contributes a different source of health risk via three exposure pathways. The health risk values of V, Cu, and Zn were mainly attributed to traffic exhaust, those of Pb were mainly related to traffic exhaust and coal combustion, those of Ni were mainly attributed to industrial exhaust, those of As were mainly related to coal combustion, and those of Mn were mainly attributed to dust and traffic exhaust. Therefore, the emission of these elements should be reduced to minimize their potential risks to human health.

4 Conclusion

The mass concentrations, chemical compositions, source apportionment, and health risk assessment of PM\textsubscript{2.5} in the rural, urban, traffic, industrial, and scenic sites of Zhengzhou were examined from February to December of 2016.

The annual mean concentration of PM\textsubscript{2.5} in these five sites was 119 µg/m\textsuperscript{3}, and the WSII\textsubscripts{s}, carbonaceous species (EC and OC), and elements accounted for 47.7%, 14.4%, and 9.6% of
the PM$_{2.5}$ concentration in Zhengzhou during the sampling period, respectively. The results of CDs indicated that the situation in DF was significantly different from that in the other sites. PM$_{2.5}$, OC, EC, and WSIs, except for F$^{-}$, Ca$^{2+}$, and Mg$^{2+}$, showed a relatively homogeneous spatial distribution. The NO$_3^{-}$/SO$_4^{2-}$ in the heavy pollution period (December 18 to 20, 2016) significantly decreased along with increasing PM$_{2.5}$ concentrations, thereby suggesting that stationary sources might have important effects on the PM$_{2.5}$ concentrations during the heavy pollution period. The annual OC/EC ratio was 8.3, which implies the possible presence of SOC.

PMF model was used to identify the six main sources of PM$_{2.5}$ in Zhengzhou, namely, dust (15.1%), coal combustion (17.6%), secondary aerosol (35.1%), vehicle traffic (17.3%), industry (7.3%), and biomass burning (7.7%). The results of the backward trajectory analysis reveal that the long-range transmission of pollutants in Zhengzhou mainly originated from the Shandong, Hubei, and Shaanxi Provinces. The results of the PSCF analysis also identified Puyang, Hebi, Xinxiang, and Kaifeng as potential sources of PM$_{2.5}$ pollutants.

The non-carcinogenic and carcinogenic risk values of all elements from the five sampling sites through ingestion and dermal pathways were higher among children than adults, while through the inhalation pathway were higher among adults than children. As and Ni have the highest carcinogenic risk while As and Pb have the highest non-carcinogenic risk for both children and adults through all three pathways. The As in HKG, ZM, XM, and SSQ can bring carcinogenic risks for children through ingestion, while in ZM, XM, and SSQ can bring carcinogenic risk for adults. Meanwhile, the Pb in all five sampling sites produces an intolerable non-carcinogenic risk for children via ingestion.
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Table Captions

Table 1. Description of PM$_{2.5}$ in the sampling sites in Zhengzhou
Table 2 Summary of PMF and error estimation diagnostics from four to nine factors.
Table 3 Contributions of PM$_{2.5}$ in five sampling sites in Zhengzhou and comparison with other city in China.
Table 1
Description of PM$_{2.5}$ in the sampling sites in Zhengzhou

<table>
<thead>
<tr>
<th>Site</th>
<th>Site code</th>
<th>Coordinates</th>
<th>Site description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forty-seventh middle</td>
<td>SSQ</td>
<td>Lat: N 34.46</td>
<td>Urban site, near Zhengzhou International Convention and Exhibition center, high</td>
</tr>
<tr>
<td>school</td>
<td></td>
<td>Lon: E 113.44</td>
<td>traffic</td>
</tr>
<tr>
<td>Hangkonggang</td>
<td>HKG</td>
<td>Lat: N 34.34</td>
<td>Traffic site, close to Xinzheng International Airport, greatly affected by aircraft</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lon: E 113.51</td>
<td>fuel</td>
</tr>
<tr>
<td>Xinmi</td>
<td>XM</td>
<td>Lat: N 34.32</td>
<td>Industrial site, adjacent to the main road (Xidajie) in Xinmi, the area is rich</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lon: E 113.19</td>
<td>in industry</td>
</tr>
<tr>
<td>Dengfeng</td>
<td>DF</td>
<td>Lat: N 34.25</td>
<td>Scenic site, located in the scenic area, about 400 meters from zheng-shao-loo</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lon: E 112.52</td>
<td>highway</td>
</tr>
<tr>
<td>Zhongmu</td>
<td>ZM</td>
<td>Lat: N 34.51</td>
<td>Rural site, far from the city, there is no obvious industrial source nearby</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lon: E 114.16</td>
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Table 2
Summary of PMF and error estimation diagnostics from four to nine factors.

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<tr>
<th></th>
<th>4 factors</th>
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<th>7 factors</th>
<th>8 factors</th>
<th>9 factors</th>
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<td>3676</td>
<td>3416</td>
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<tr>
<td>Q_{Robust}</td>
<td>33711</td>
<td>27756</td>
<td>22706</td>
<td>18723</td>
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<td>Q_{True}</td>
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<td>26521</td>
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<tr>
<td>Q_{true}/Q_{exp}</td>
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<td>8.81</td>
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<td>4.89</td>
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<tr>
<td>Q_{robust}/Q_{expected}</td>
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<tr>
<td>Factor with BS mapping</td>
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<td>factor 4,</td>
<td>all factors &gt;</td>
<td>all factors &gt;</td>
<td>factor 1,</td>
<td>factor 9,</td>
</tr>
<tr>
<td>Year</td>
<td>%</td>
<td>Coal combustion</td>
<td>Biomass combustion</td>
<td>Vehicular traffic</td>
<td>Industrial Dust</td>
<td>Secondary aerosol</td>
</tr>
<tr>
<td>--------------</td>
<td>--------</td>
<td>-----------------</td>
<td>--------------------</td>
<td>-------------------</td>
<td>-----------------</td>
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<tr>
<td>HKG</td>
<td>15.9 ± 13.2</td>
<td>6.6 ± 3.8</td>
<td>18.6 ± 11.0</td>
<td>8.2 ± 3.4</td>
<td>17.5 ± 16.9</td>
<td>33.2 ± 23.9</td>
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<td>ZM</td>
<td>18.4 ± 17.8</td>
<td>10.7 ± 6.1</td>
<td>15.8 ± 13.1</td>
<td>5.4 ± 3.0</td>
<td>14.8 ± 12.7</td>
<td>35.0 ± 21.2</td>
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<td>XM</td>
<td>20.4 ± 14.5</td>
<td>7.6 ± 5.3</td>
<td>13.4 ± 15.0</td>
<td>11.4 ± 11.1</td>
<td>13.7 ± 14.8</td>
<td>33.4 ± 21.8</td>
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<td>SSQ</td>
<td>16.5 ± 5.4</td>
<td>5.7 ± 3.6</td>
<td>22.1 ± 15.5</td>
<td>4.2 ± 2.4</td>
<td>18.2 ± 15.5</td>
<td>33.3 ± 18.1</td>
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<tr>
<td>DF</td>
<td>16.3 ± 10.8</td>
<td>7.3 ± 5.1</td>
<td>16.5 ± 9.8</td>
<td>7.2 ± 6.9</td>
<td>10.7 ± 9.1</td>
<td>42.0 ± 21.0</td>
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<td>21.1 ± 17.0</td>
<td>8.1 ± 4.8</td>
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<td>7.8 ± 7.7</td>
<td>11.1 ± 13.6</td>
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<td>Spring</td>
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<td>21.3 ± 18.3</td>
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<td>Summer</td>
<td>17.5 ± 15.7</td>
<td>5.3 ± 4.6</td>
<td>17.4 ± 17.8</td>
<td>5.8 ± 4.9</td>
<td>12.1 ± 10.3</td>
<td>41.9 ± 19.7</td>
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<td>Autumn</td>
<td>16.5 ± 9.0</td>
<td>9.6 ± 6.2</td>
<td>16.2 ± 10.6</td>
<td>8.1 ± 8.3</td>
<td>15.8 ± 11.8</td>
<td>33.7 ± 16.0</td>
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<tr>
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**Table 3**
Contributions of PM$_{2.5}$ in five sampling sites in Zhengzhou and comparison with other cities in China.
Figure Captions

Fig. 1 Location of five sample sites.

Fig. 2 Temporal variations of PM2.5 concentrations in five sampling sites in Zhengzhou, MEPC: Ministry of Environmental Protection of China. (D: daytime; N: night)

Fig. 3 CDs of different chemical species for five sites in Zhengzhou.

Fig. 4 Scatter plots of AE versus CE in four seasons in Zhengzhou. Different colors correspond to different concentrations of PM2.5.

Fig. 5 Scatter plots of (a) NH$_4^+$ versus SO$_4^{2-}$ and (b) NH$_4^+$ versus [SO$_4^{2-}$ + NO$_3^-$] in Zhengzhou. Different colors correspond to different concentrations of PM$_{2.5}$.

Fig. 6 Average compositional fractions (%) of PM$_{2.5}$ in five sites and heavy pollution days (December 18-20, 2016) in Zhengzhou. (TE: total elements)

Fig. 7 Source profiles of PM$_{2.5}$ obtained by PMF model analysis in Zhengzhou.

Fig. 8 The results of 48-hour backward air trajectories for December18-20, 2016 arrived at five sampling sites in Zhengzhou and the altitude was set at 500m.

Fig. 9. Spatial distributions of PSCF for PM2.5 at SSQ site.
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Fig. 2 Temporal variations of PM$_{2.5}$ concentrations in five sampling sites in Zhengzhou, MEPC: Ministry of Environmental Protection of China. (D: daytime; N: night)
Fig. 3 CDs of different chemical species for five sites in Zhengzhou.

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*Fig. 3 CDs of different chemical species for five sites in Zhengzhou.*
Fig. 4 Scatter plots of AE versus CE in four seasons in Zhengzhou. Different colors correspond to different concentrations of PM$_{2.5}$. 

Winter: $y = 0.73x + 0.36$ \[R^2 = 0.94\]

Spring: $y = 0.92x + 0.21$ \[R^2 = 0.89\]

Summer: $y = 1.21x + 0.07$ \[R^2 = 0.76\]

Autumn: $y = 0.91x + 0.17$ \[R^2 = 0.89\]
Fig. 5 Scatter plots of (a) NH$_4^+$ versus SO$_4^{2-}$ and (b) NH$_4^+$ versus \([SO_4^{2-} + NO_3^-]\) in Zhengzhou. Different colors correspond to different concentrations of PM$_{2.5}$. 

(a) \(y = 1.65x + 0.12\) \(R^2 = 0.90\) 

(b) \(y = 0.83x + 0.15\) \(R^2 = 0.95\)
Fig. 6 Average compositional fractions (%) of PM$_{2.5}$ in five sites and heavy pollution days (December 18-20, 2016) in Zhengzhou. (TE: total elements)
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