CrossMark

Assessment of heavy metal characteristics and health risks associated with PM$_{2.5}$ in Xi'an, the largest city in northwestern China

Pingping Liu[1] · Huarui Ren[1] · Hongmei Xu[1,2] · Yali Lei[1] · Zhenxing Shen[1]

Abstract

Fine particulate matters (PM$_{2.5}$) samples were collected in Xi'an, northwestern China, from May 2015 to April 2016. The concentrations, seasonal variations, potential sources, and health risks for personal exposure for ten metallic elements (i.e., Ba, Zn, Cu, As, Ni, Pb, Mn, Cr, Cd, and Hg) bounded to PM$_{2.5}$ were determined and assessed in this study. The results showed that the average PM$_{2.5}$ mass concentration in Xi'an was 62.1 ± 35.0 μg m^{-3} during the sampling period. The annual concentration of the total quantified elements was 2459.5 ± 1789.8 ng m^{-3}, with relatively higher values in winter (3334.9 ± 1690.9 ng m^{-3}) and spring (2809.4 ± 2465.4 ng m^{-3}), in comparison of those in summer (1857.6 ± 1162.7 ng m^{-3}) and autumn (1252.5 ± 842.4 ng m^{-3}). Two elements of Ba (678.0 ± 684.9 ng m^{-3}) and Zn (1264.8 ± 725.3 ng m^{-3}) had greater fluctuations in concentrations and were accounted for more than 80% of the concentration of total quantified elements for each season. The concentrations of As in Xi'an exceeded the national standard in China. The enrichment factors (EFs) of most target heavy metals were high, exceeding 100 for Zn, As, Pb, Cd, and Hg, attributed to strong influences from human activities. Moreover, the largest enrichment of heavy metals in PM$_{2.5}$ occurred in Xi'an in winter. Principle component analysis (PCA) was applied for source apportionment. Coal and other fuel combustion, vehicle exhaust, and industrial activities were the three major pollution sources which contributed 43.6, 29.9, and 15.3%, respectively, of the total variance of PM$_{2.5}$. The health risk assessment showed that the non-cancer risks of As, Pb, and Cr for children were greater than 1, as well as of As for adults. The cancer risks of As and Cr were higher than 1×10^{-6}, indicating that the two elements had high potentials for both non-cancer and cancer risks. Our finding suggests that the PM$_{2.5}$ and related heavy metal pollutions in Xi'an were serious and posed high potential health risks. Effective controls and measures should be established in the studied area.

Keywords PM$_{2.5}$ · Heavy metals · Source apportionment · Health risk assessment · Xi'an

Introduction

In recent years, the increase of PM$_{2.5}$ (particulate matter with aerodynamic diameter equal to or less than 2.5 μm)

✉ Hongmei Xu
xuhongmei@xjtu.edu.cn

[1] Department of Environmental Science and Engineering, Xi'an Jiaotong University, No. 28 Xianning West Road, Beilin Zone, Xi'an 710049, China

[2] Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control (AEMPC), Nanjing University of Information Science & Technology, Nanjing, China

concentration in the atmosphere affects the air quality in northwestern China and causes frequent haze events occurred in winter (Shen et al. 2017; Kan et al. 2012; Chen et al. 2015; He et al. 2014). PM$_{2.5}$ can adhere to a variety of toxic substances, such as carbonaceous aerosols (e.g., organic pollutants), microorganisms (i.e., bacteria and viruses), and particularly heavy metals (Witkowska et al. 2016; Khan et al. 2017). Heavy metals in PM$_{2.5}$ have attracted widespread concerns. They would be accumulated after entering the human body which can neither be digested nor decomposed in most cases, leading to strong impacts on human health and even being linked to cancer after reaching a certain dose. For example, Pb can cause severe blood and neuropathic lesions in children (Hu et al. 2012; Zheng et al., 2010; Chen et al. 2014). Ni is also found to be carcinogenic and even harm the nervous and reproductive systems of humans (Xu et al. 2017).

The concentrations of PM$_{2.5}$-bounded heavy metals in Asia were often above the natural background levels owing to a

variety of anthropogenic processes, thus presenting high potential toxicities (Charlesworth et al. 2011; Fang et al. 2010; Wei and Yang 2010). Cao et al. (2012) reported that the average $PM_{2.5}$ concentrations were > 100 μg m^{-3} in 14 Chinese large cities. The maximum of 356 μg m^{-3} was found in Xi'an during winter in 2003, in which the Pb level reached an average of 1.68 μg m^{-3}. Wang et al. (2015) collected aerosol samples at the urban and rural regions of Xi'an in 2010, showing that the annual average Pb concentration was 0.3 ± 0.3 μg m^{-3}. Summarizing the literatures listed above, even though the $PM_{2.5}$ and its heavy metal pollutions in Xi'an have been improved, the air quality does not meet the standards established by World Health Organization (WHO) (WHO 2006) or the Chinese Government (GB 3095–2012 2012).

The mechanism of haze formation and the health risks associated with heavy metals in $PM_{2.5}$ are still unclear. Apportionment on the pollution sources can provide information regarding the improvement of urban air quality and public health (Liu et al. 2014). The source of heavy metals in $PM_{2.5}$ can be divided into two main categories: natural and anthropogenic sources. Natural sources mainly include soil dusts, forest fires, volcanic eruptions, sea salt particles, and microorganisms (Wang et al. 2005; Vallius et al. 2005; Wang et al. 2013; Chen et al. 2002). Anthropogenic sources refer to combustions of fossil fuels, emissions from industrial enterprises, exhausts of motor vehicles, and fugitive dusts related to human activities. Okuda et al. (2008) showed that the coal-fired emission is one of the major sources of As, Pb, and Cd. The elements of Ni, Pb, Cu, Cr, Cd can be emitted into the environment from road dusts, tire wearing from ground friction, and vehicle braking system. Manalis et al. (2005) confirmed that the surface coating of automotive components and the wears of rubber products can produce $CrPbO_4$ particles. In addition, traffic emissions contribute significantly to atmospheric Zn, Cu, and Ba (Adachi and Tainosho 2004). Meng et al. (2009) found that Pb, As, and Cd in PM originated mainly from industrial emissions. Moreover, there are many other sources for heavy metals in $PM_{2.5}$ such as waste incineration, which discharge Ni, Zn, Hg, As, Cr, Cu, Mn, and Pb to the environment (Adachi and Tainosho 2004; Meng et al. 2009; Hu et al. 2003; Jodeh et al. 2018).

According to the guideline established by United States Environmental Protection Agency (USEPA), As, Ni, Pb, Cr, and Cd are classified as carcinogenic metals (USEPA 1996; USEPA 2001; USEPA 2007). Du et al. (2012) conducted a health risk assessment by analyzing the mass concentrations and characteristics of As, Cr, Cd, Ni, Zn, Pb, Hg, Cu, and Mn in $PM_{2.5}$ in Shenzhen, southeastern China. The results showed that the carcinogenic risks of those heavy metals through the respiratory pathway were close to the acceptable level, while the highest were seen for Cr and As. There was a late start of health risk studying on exposure to $PM_{2.5}$-bounded heavy metal in more-polluted northwestern China, compared with

developed eastern regions. The researches related to this area are still very limited (Liu et al. 2014; Qiu et al. 2018). However, there is an urgent need for the assessment in Xi'an owing to the heavy pollutions. The main objectives of this study are to (1) determine $PM_{2.5}$ elemental concentrations and seasonal variations in Xi'an; (2) identify the potential sources of the heavy metals by using enrichment factors, correlation analysis, and principal component analysis (PCA); and (3) assess the health risks of heavy metals via ingestion, dermal contact, and inhalation pathways. The results of the present study could provide the information about the sources and the potential risks associated with heavy metals in $PM_{2.5}$ that is useful for control the $PM_{2.5}$ pollution in Xi'an, and even in northwestern China.

Material and methods

Site description and $PM_{2.5}$ sampling

Xi'an (~ 10,108 km^2) is located in the center of Guanzhong Plain, which is at the southern edge of the Loess Plateau in northwestern China. There was approximately 8.83 million inhabitants in 2016. The sampling site (34.23° N, 108.98° E) was set up at the southeastern area of downtown Xi'an (Fig. 1) and surrounded by residential areas, a school campus, and heavy traffic roads. Twenty-four-hour integrated $PM_{2.5}$ samples (from 10:00 a.m. to 10:00 a.m. the next day, local time) were collected from May 2015 to April 2016 every 3 days. The $PM_{2.5}$ were collected onto pre-combustion (at 800 °C, 3 h) quartz-fiber filters (20.3 cm × 20.4 cm) using a high-volume air sampler (HVS-$PM_{2.5}$, Thermo Fisher Scientific, Waltham, MA, USA) with a flow rate of 1.1 m^3 min^{-1}. There was a total of 112 valid filter samples. All loaded samples were stored in a freezer at − 4 °C to prevent any evaporation of volatile compounds until chemical analysis. Besides, a field blank for each season (i.e., a total of four blanks) was collected which was analyzed the same way as the samples. All the concentrations reported afterward have been corrected with the values of field blanks. In this study, the months of December, January, and February were divided into winter, while other seasons were deferred successively. Air temperature, wind speed and direction, atmospheric pressure, and relative humidity (RH) were obtained from the daily updated data of the China State Meteorology Bureau, China weather network: http://www.weather.com.cn/ (Table S1).

Analytical methods

$PM_{2.5}$ masses were obtained by gravimetric method that the filters were weighed in a pre-conditioned chamber (at a temperature of 20–23 °C and RH of 35–45% for 24 h) before and after the sampling. A Sartorius LA130 S-F electronic microbalance (sensitivity: ± 0.10 mg, Sartorius, Gottingen, Germany) was
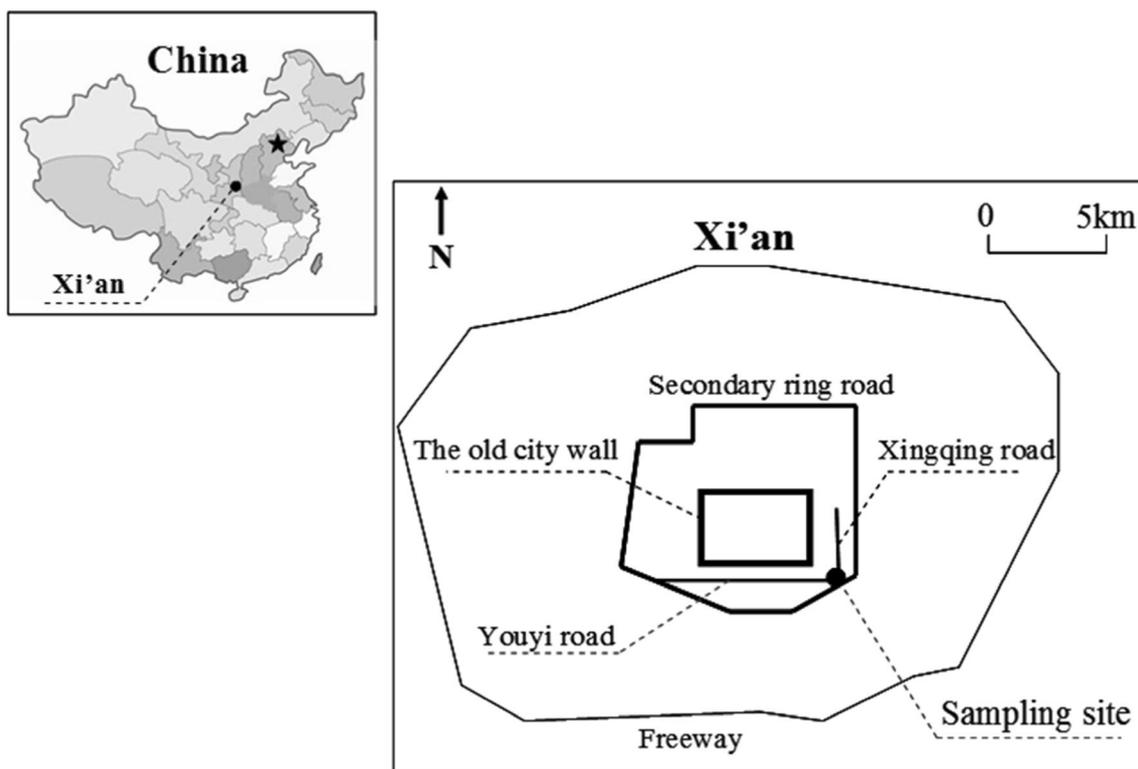
Fig. 1 A map shown the location of sampling site

used to weight the filters. A 47-mm diametral punch was cut from the parent sample for analysis of ten heavy metals (i.e., Ba, Zn, Cu, As, Ni, Pb, Mn, Cr, Cd, and Hg) plus one additional element of Fe, which is a representative of the earth's crust. One quarter of the punch (an area of 4.34 cm^2) was cut into small pieces and placed into a Teflon vessel for acid digestion. Each sample was added with 6 mL of a mixture of HNO_3:HCl (1:3 v/v) and 1 mL hydrofluoric acid (HF). The vials were screwed on the digestion tank and stood for 30 min, and then placed into a microwave digestion unit (Multiwave Go, Anton Paar, Graz, Austria). The digestion temperatures gradually increased to 120, 160, 180, and 200 °C in 45 min. After digestion, the solution was boiled on a hot plate (120 °C) until its volume was reduced to 1 mL. The digested solution was then diluted to 10 mL with deionized water (resistivity = 18.3 MΩ-cm) (Liu et al. 2017a). After filtering of filter debris (Nylon 66, 0.22 μm, Jinteng), the solution was then analyzed for elemental concentrations by an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Shimadzu, Kyoto, Japan). The recoveries of the measured elements ranged from 80 to 120% (GBW07401–GBW07408 2003). The data reported in this study were not corrected by recoveries.

Source identification

In this study, qualitative analyses of the elemental sources in PM$_{2.5}$ were evaluated by correlation analysis and enrichment factor (EF). Pearson's correlation analysis can identify elements from the same pollution source, and further determine this source (Liu et al. 2017b; Lee and Allen 2012; Oliva and Espinosa 2007). Elemental correlation analysis was conducted by SPSS software (Model 19.0).

The EF of each element was calculated relative to a reference crustal element of Fe (a good indicator for crustal material due to being less affected from anthropogenic pollution) (Taylor and Mclennan 1995) by the following equation:

$$EF = (X/Fe)_{aerosol}/(X/Fe)_{crust} \qquad (1)$$

where EF is the enrichment factor of target element X, $(X/Fe)_{aerosol}$ is the concentration ratio of X to Fe in PM$_{2.5}$ samples, and $(X/Fe)_{crust}$ is the average concentration ratio of X to Fe in

Table 1 PM$_{2.5}$ mass concentration (μg m^{-3}) and exceeding standard rate (%) in each season in Xi'an during the sampling period

Season	PM$_{2.5}$ mass concentration (μg m^{-3})	Standard exceeding rate (%)
Spring	78.4 ± 52.7	28
Summer	45.6 ± 21.1	11
Autumn	40.2 ± 30.6	18
Winter	78.5 ± 22.6	56
Annual	62.1 ± 35.0	31

crustal dust. If EF ranges from 1 to 10, the element X can be considered to originate mainly from soil; if EF > 10, the element X mainly originated from human activities (Taylor and Mclennan 1995; Han et al. 2006).

Principal component analysis

PCA applies dimension reduction methods, converting multiple indicators into significant representative indicators without damaging the original data (Han et al. 2006; Jiao et al. 2013). It has been widely applied to identify heavy metal pollution sources in $PM_{2.5}$ (Zhang and Wang 2009; Ajmone et al. 2008). In current research, SPSS software (Model 19.0) was used to run PCA to characterize the potential sources. PCA was conducted with varimax rotation and each factor contained information of metals combined into independent variables, while the values represent the relative contribution of each metal to the score (Han et al. 2006; Zhang and Wang 2009). In this study, PCA extracted four main factors; the total variation rate was higher than 96%, covering the main sources of heavy metals in $PM_{2.5}$ in Xi'an.

Health risk assessment model

This study adopted a health risk assessment model from the U.S.EPA to evaluate health risks of elements in $PM_{2.5}$ (USEPA 2011). $PM_{2.5}$ causes health risks to receptors mainly in three ways: direct hand-mouth ingestion (D_{ing}), inhalation through mouth and nose (D_{inh}), and dermal contact (D_{dermal}). The average daily dose (D, unit: mg kg^{-1} day^{-1}) for each exposure pathway can be calculated as the following formulas (Kong et al. 2012; Liu et al. 2017a; USEPA 1989; Kong et al. 2015; Ferreira and De 2005):

$$D_{ing} = C(mg/kg) \times \frac{IngR \times EF \times ED}{BW \times AT} \times 10^{-6} \tag{2}$$

$$D_{inh} = C(mg/kg) \times \frac{InhR \times EF \times ED}{PEF \times BW \times AT} \tag{3}$$

$$D_{dermal} = C(mg/kg) \times \frac{SA \times SL \times ABS \times EF \times ED}{BW \times AT}$$
$$\times 10^{-6} \tag{4}$$

The exposure parameters above were listed in Table S2 (Liu et al. 2017a). The non-cancer risk of all elements through the three pathways can be evaluated by hazard quotient (HQ) and hazard index (HI) (USEPA 1989; Liu et al. 2017a). The cancer risk of five elements (i.e., As, Ni, Pb, Cr, and Cd) in this study via inhalation is calculated by the increased lifetime cancer risk (ILCR) (Kong et al. 2012; Kong et al. 2015; Liu et al. 2017a). C in Eqs. (2)–(4) refers to the upper limit of the 95% confidence interval (95% UCL) of the average concentration of each element, which is also considered as the estimate of the "reasonable maximum exposure". In this study, $C_{95\%UCL}$ was calculated by the SPSS software (Model 19.0).

Quality assurance and quality control

The filters were folded, then packed with aluminum foil after the sampling. Each filter was weighed three times before and after sampling and the average value was reported in this study. All the glassware and filter assembly were acid-washed and oven-dried to avoid contamination among samples. Reference materials (Soil Standard Series: GBW 07408 for ocher and GBW 07404 for calcareousness, produced by National Research Center for Certified Reference Materials, China) was applied to verify the feasibility of the analytical method in this study. The recoveries of metal elements in the loess and coal fly ash source samples were between 80 and 120%, demonstrating that our experimental approach offers a feasible and complete digestion (GBW07401–GBW07408 2003). Each batch of samples was analyzed with at least two laboratory blanks to identify the accuracy of the method. One $PM_{2.5}$ sample was analyzed twice per ten samples to assure the relative errors, which were less than 20% for all target elements (Kong et al. 2011).

Results and discussion

Characteristics of $PM_{2.5}$ and its elements

$PM_{2.5}$ daily and annual guidelines are 75 and 35 μg m^{-3} (secondary standard) established by the Ambient Air Quality Standard of China, respectively (AAQS, GB 3095–2012 2012). The annual average concentration of $PM_{2.5}$ in Xi'an was 62.1 ± 35.0 μg m^{-3}, which exceeded 1.8 times of the AAQS. Seasonal $PM_{2.5}$ mass concentrations and exceeding standard rates are shown in Table 1. The concentrations had a descending rate of winter > spring > autumn > summer. The mean $PM_{2.5}$ mass concentration in winter was close to that in spring, but with much higher exceeding standard rate. This is attributed with the larger variations on the $PM_{2.5}$ mass concentration in winter, while extremely high values were shown in few sampling days. Along the Spring Festival period (i.e, seven consecutive public holidays in winter), the $PM_{2.5}$ concentrations reduced sharply and almost met the AAQS (GB 3095–2012), resulting from shutdowns of factories and decreases of other anthropogenic $PM_{2.5}$ emissions on holidays (Cao et al. 2012; Kong et al. 2015). The $PM_{2.5}$ exceeding the standard rate was relatively lower in summer and autumn than the other two seasons that benefited from favorable meteorological conditions. More precipitation and higher wind speed were conducive to the diffusion and dispersion of PMs (Xu et

Table 2 Mass concentrations of measured elements (ng m^{-3}) in PM$_{2.5}$ in different seasons

Elements	Spring (n = 18)		Summer (n = 36)		Autumn (n = 17)		Winter (n = 41)		Annual Average ± STD*
	Range	Average ± STD*	Range	Average ± STD*	Range	Average ± STD*	Range	Average ± STD*	
Ba	20.3–5330.5	865.6 ± 888.7	9.2–2757.1	686.2 ± 562.4	19.0–990.1	242.8 ± 233.5	29.6–3837.9	768.7 ± 845.3	678.0 ± 684.9
Zn	369.2–4522.6	1455.2 ± 942.6	4.7–4172.9	840.8 ± 408.9	39.0–1514.6	650.2 ± 373.5	400.1–5761.7	1808.4 ± 645.4	1264.8 ± 725.3
Cu	7.5–79.0	29.7 ± 14.6	1.8–54.1	22.2 ± 10.3	1.9–104.8	40.2 ± 30.0	4.1–152.4	69.3 ± 29.3	43.4 ± 28.0
As	38.1–452.2	141.7 ± 66.9	7.4–249.1	89.0 ± 42.8	6.8–223.7	68.4 ± 34.1	93.7–427.1	173.9 ± 47.6	125.4 ± 59.3
Ni	8.9–84.6	24.9 ± 12.6	1.2–37.1	14.1 ± 5.8	1.2–54.1	12.9 ± 7.5	11.5–76.3	30.0 ± 10.2	21.5 ± 10.8
Pb	25.6–257.6	111.0 ± 57.2	6.1–213.2	87.3 ± 44.1	9.1–357.2	146.9 ± 103.0	13.9–721.9	247.9 ± 104.0	159.0 ± 98.2
Mn	19.1–195.3	68.9 ± 33.2	4.3–135.4	43.6 ± 20.8	3.7–138.2	34.0 ± 18.6	40.2–222.5	85.4 ± 28.7	61.5 ± 30.3
Cr	33.3–273.1	108.0 ± 68.8	0.6–254.6	71.5 ± 33.2	3.5–130.5	53.0 ± 24.6	36.2–496.3	143.5 ± 55.7	100.9 ± 55.1
Cd	0.4–4.9	2.3 ± 1.2	0.1–4.8	1.6 ± 0.8	0.1–8.5	3.0 ± 2.2	0.4–14.3	5.2 ± 2.3	3.3 ± 2.1
Hg	0.6–6.4	2.1 ± 1.0	0.1–4.0	1.3 ± 0.6	0.1–4.3	1.1 ± 0.6	1.1–5.8	2.6 ± 0.7	1.9 ± 0.9

*STD: standard deviation

al. 2018). However, in autumn, the PM$_{2.5}$ exceeding the standard rate was slightly higher than that in summer. It is because biomass combustion could emit a large amount of PM$_{2.5}$ in the surrounding rural areas of Xi'an during this period (Zheng et al. 2005; Rastogi et al. 2014).

Each element concentration in PM$_{2.5}$ is presented in Table 2. The annual average concentration of measured elements was 2459.5 ± 1789.8 ng m^{-3} in Xi'an during the whole year, with the concentrations of 3334.9 ± 1690.9 ng m^{-3} in winter, 2809.4 ± 2465.4 ng m^{-3} in spring, 1857.6 ± 1162.7 ng m^{-3} in summer, and 1252.5 ± 842.4 ng m^{-3} in autumn. Elevated elemental concentrations were observed in winter, because Xi'an is affected by the high pressure of the cold zone and other unfavorable weather conditions in winter (Zhen 2015). Coal combustion used for heating in winter is an important seasonal emission source of heavy metals in Xi'an (Cao et al. 2012; Xu et al. 2018). Moreover, cold weather leads to a "cold start" to the motor vehicles, which makes PM$_{2.5}$ heavy metal levels in automobile exhaust emissions more obvious in winter (China Statistical Yearbook 2017). Sources and sinks mentioned above cause higher PM$_{2.5}$ heavy metal concentrations in winter than that in spring, and much higher than other seasons.

Figure 2 shows the monthly variations in PM$_{2.5}$ and ten elemental mass concentrations in Xi'an from May 2015 to April 2016. In Fig. 2a, the PM$_{2.5}$ mass concentrations showed a great deviation in March 2016, mainly due to the large fluctuation of emission sources around the sampling site, especially with influences from dust storm during springtime (Wang et al. 2013). The lowest monthly PM$_{2.5}$ concentration and associated elements were observed in October 2015, when the abundant precipitation occurred in this month that can be proved by the meteorological data. As our best knowledge, the precipitation in autumn is usually high in Xi'an, accounting for 32.4% of the annual precipitation (Deng 2008). After October, the temperature drops rapidly in most of the northern Chinese city, leading to large-scale coal combustion for heating. This is consistent with our result that the peak elemental concentrations were seen in February 2016.

The annual average concentrations of elements showed a descending order of Zn > Ba > Pb > As > Cr > Mn > Cu > Ni > Cd > Hg. Zn accounted for more than half of the total quantified elements, while Ba contributed for one third. The concentrations of these elements varied greatly but were in high compositions during the entire period. The average concentrations of As, Pb, and Cr were in the same levels among the four seasons, accounting for 3.5–10% of the total quantified elements. The compositions of Cu, Ni, Cd, and Hg were less than 1%. According to the AAQS, the annual average concentration of As exceeded the standard (6 ng m^{-3}) while Cd, Hg, and Pb met the guidelines (5, 50, and 500 ng m^{-3}, respectively) (GB 3095–2012 2012).
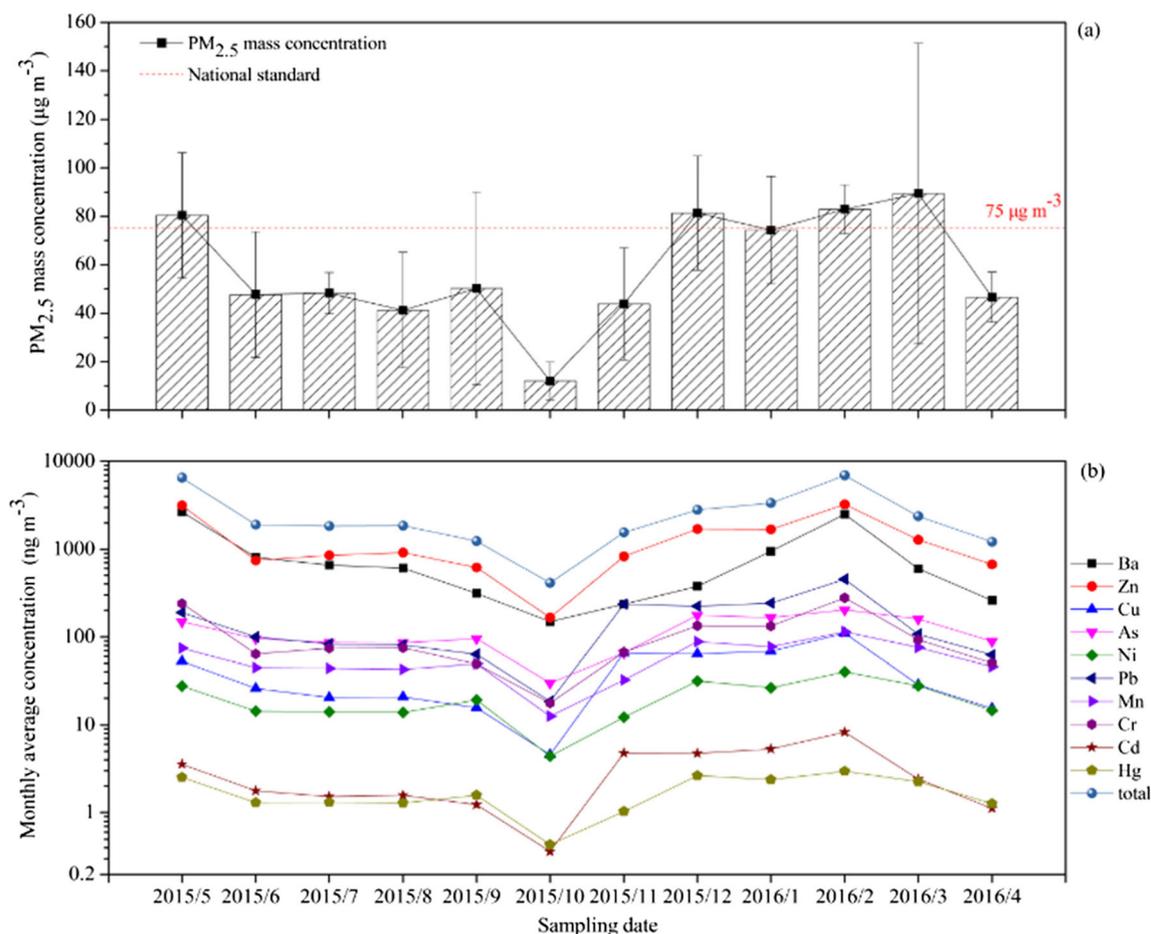
Fig. 2 Monthly average concentrations of (**a**) $PM_{2.5}$ ($\mu g\ m^{-3}$) and (**b**) ten elements ($ng\ m^{-3}$) in Xi'an during the sampling period

Source of elements in $PM_{2.5}$

In order to investigate the inter-relationships for the elements in $PM_{2.5}$ and to determine their sources and transmission pathways in $PM_{2.5}$, Pearson's correlation analysis was applied and its results ($P < 0.05$) are presented in Table 3. Zn and Cr were strongly correlated with each other, suggesting their origins

from the same emission sources such as metal smelting and industrial activities. In a previous study, the authors proved that Cu, Co, Cr, and Zn could be emitted from industrial activities since they were positively correlated with each other in road dust samples collected in Turkey (Tokalioglu and Kartal 2006). In addition, significant correlations among Cu, Pb, and Cd indicated that these elements were both from vehicle

Table 3 Pearson's correlation matrix of targeted heavy metals in $PM_{2.5}$

Elements	Ba	Zn	Cu	As	Ni	Pb	Mn	Cr	Cd	Hg
Ba	1.000									
Zn	0.116	1.000								
Cu	−0.069	0.311	1.000							
As	0.275	0.091	0.153	1.000						
Ni	0.243	0.111	0.182	0.847	1.000					
Pb	−0.103	0.304	0.871	0.101	0.133	1.000				
Mn	0.269	0.052	0.167	0.849	0.865	0.109	1.000			
Cr	0.184	0.824	0.352	0.121	0.141	0.341	0.088	1.000		
Cd	−0.072	0.387	0.843	0.196	0.223	0.825	0.205	0.405	1.000	
Hg	0.251	0.084	0.174	0.845	0.856	0.129	0.848	0.118	0.217	1.000

Fig. 3 Enrichment factors (EFs) relative to UCC (the Earth's upper continental crust in Taylor and Mclennan 1995) for elements in PM$_{2.5}$ collected in Xi'an in different seasons
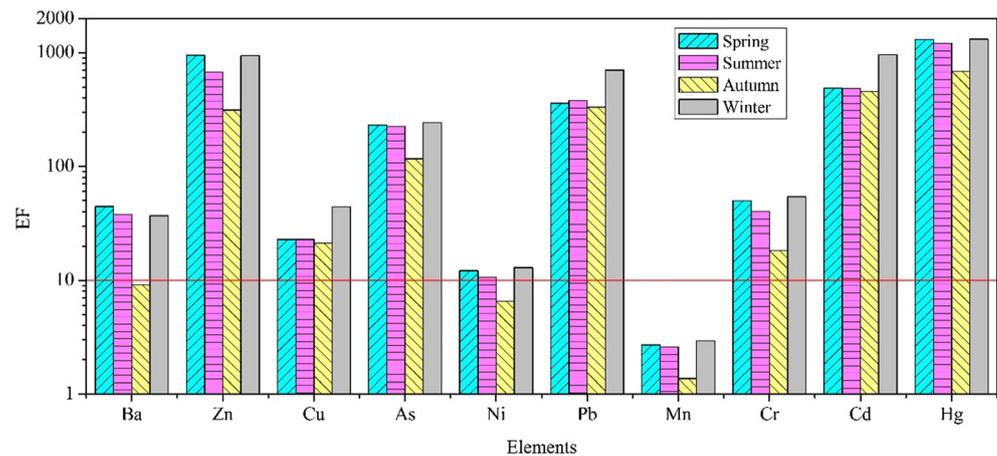
emissions and industrial activities. Cd and Cu are good indicators of contamination in soils and markers of traffic emission (Kong et al. 2012). As and Hg are signatures of emissions from coal combustion and fossil fuels as well (Lu et al. 2009). Ni and Mn were all correlated with As and Hg significantly, indicating that they were affected by the coal-fired source emissions.

The enrichment factors (EFs) of elements in different seasons are shown in Fig. 3. The EFs were characterized by very high values in winter and slightly high values in autumn. In winter, emissions from coal-fired plants and high air pressure (i.e., unfavorable diffusion of heavy metals) both caused the severe heavy metal enrichments. The EFs of the target elements had the same order of Hg > Cd > Zn > Pb > As > Cr > Cu > Ba > Ni > Mn in each season, except Cu > Ba in winter. Among them, EFs of Zn, As, Pb, Cd, and Hg exceeded 100 (with average values of 726.6, 226.3, 491.7, 693.1, and 1233.1, respectively), which almost all originated from anthropogenic sources. Although the concentrations of Hg were relatively low, its EF was the highest one, with the annual average value of > 1000, indicating the heavy Hg pollution in Xi'an (Cao et al. 2012). The EFs of Cu, Cr, and Ni were 31.7, 40.6, and 11.5, respectively. These elements are emitted to the environments from both natural and anthropogenic sources. The EF of Mn was the lowest one (with an average of 2.6), potentially ascribed with the fact that Mn mainly originated from natural sources.

Principal component analysis for source apportionment

The results of source apportionment with the elements in PM$_{2.5}$ using PCA are shown in Table 4. Factor 1 accounted for 43.6% of total variance. As, Ni, and Hg had the highest values (0.86, 0.88, and 0.87, respectively) in this factor, representing a contribution from anthropogenic sources, such as coal and other fossil fuel combustions (Cao et al. 2012; Lu et al. 2009). Factor 2 accounted for 29.9% of total variance.

Cu, Pb, and Cd (0.72, 0.75, and 0.71, respectively) are dominated in this factor, indicating the contributions of vehicle emissions and industrial activities (Kong et al. 2012). For factor 3, Zn and Cr displayed the highest values (0.71 for both), suggesting the contributions from iron and steel industry and metal smelting (Tokalioglu and Kartal 2006; Kong et al. 2012). In a word, attention should be paid to the dominant sources of coal and other fuel combustions, vehicle exhausts, and industrial activities in Xi'an. Lin et al. (2016) showed that building emission and coal burning (45.0%), vehicle emission (12.2%), and smelting chemical production (9.6%) were common sources to the PM$_{2.5}$-bounded heavy metals in Nanchang, China, in autumn 2013. They further characterized that As and Hg were mainly from coal combustion; Cu, Fe, Pb, and Co mainly came from traffic-related sources; and Zn was influenced by metal smelting. Our results are thus consistent with the elemental correlations and EF analyses conducted by the previous studies.

Table 4 Principal component analysis (PCA) of elements in PM$_{2.5}$ collected in Xi'an in 2015–2016

Elements	Principal components			
	Factor 1	Factor 2	Factor 3	Factor 4
Ba	0.262	−0.252	0.455	0.812
Zn	0.384	0.506	0.714	−0.229
Cu	0.572	0.722	−0.335	0.144
As	0.857	−0.467	−0.026	−0.068
Ni	0.876	−0.439	−0.037	−0.101
Pb	0.525	0.749	−0.344	0.130
Mn	0.858	−0.474	−0.070	−0.053
Cr	0.427	0.503	0.710	−0.149
Cd	0.611	0.706	−0.268	0.081
Hg	0.865	−0.450	−0.054	−0.081
% of variance	43.6	29.9	15.3	8.0

Table 5 Non-cancer risks for each element via three exposure pathways

Elements	HQ$_{ing}$*		HQ$_{inh}$*		HQ$_{dermal}$*	
	Adults	Children	Adults	Children	Adults	Children
Ba	2.89E−02	2.31E−01	8.76E−06	1.33E−05	3.76E−02	3.56E−02
Zn	3.27E−02	2.62E−01	9.93E−06	1.51E−05	1.49E−02	1.41E−02
Cu	9.11E−03	7.29E−02	2.55E−06	3.87E−06	1.62E−02	1.53E−02
As	3.17E + 00	2.54E + 01	9.63E−04	1.46E−03	7.07E−01	6.69E−01
Ni	8.22E−03	6.58E−02	2.42E−06	3.68E−06	1.50E−02	1.42E−02
Pb	3.53E−01	2.82E + 00	1.06E−04	1.62E−04	2.15E−01	2.03E−01
Mn	1.00E−02	8.00E−02	1.02E−02	1.55E−02	1.79E−02	1.69E−02
Cr	1.56E−01	1.25E + 00	8.26E−03	1.26E−02	2.84E−01	2.69E−01
Cd	2.55E−02	2.04E−01	2.58E−05	3.92E−05	4.65E−02	4.40E−02
Hg	4.67E−02	3.73E−01	5.55E−05	8.43E−05	6.09E−02	5.76E−02

*HQ$_{ing}$, HQ$_{inh}$ and HQ$_{dermal}$ represent the hazard quotient (HQ) calculated through hand-mouth ingestion, inhalation and dermal contact pathway, respectively

Health risk assessment of elements in PM$_{2.5}$

According to the calculated personal exposure doses of ten elements from different exposure pathways, the exposure dose from hand-mouth ingestion was much more than dermal contact and respiratory inhalation for both children and adults. Average daily exposure levels for children were higher than adults for both ingestion and inhalation exposure pathways, but reversely for dermal contact.

In the following discussion, the non-cancer risk indicator of *HI* refers to the sum of HQ via three exposure pathways (shown in Table 5 and Fig. 4). The *HI* levels were greater than 1.0 (i.e., 5.1 for adults and 31.4 for children), indicating that the elements of PM$_{2.5}$ in Xi'an can pose serious adverse non-cancer health effects. The risk for children was higher than that for adults, representing that children are more sensitive to non-cancer effects and should be minimized for their exposures to the potential sources. The non-cancer risk

levels of As for both adult and children (3.9 and 26.1, respectively) were higher than 1 (i.e., an international threshold), indicating that exposure to As is an acute health concern particularly for children in Xi'an. Since the accumulative properties of HQ were from the hand-mouth ingestion, this easily leads hazard risks of Pb and Cr for children. Pb and Cr showed fair non-cancer risks for children (3.5 and 1.5, respectively). Other elements such as Ba, Zn, Cu, Ni, Mn, Cd, and Hg conformed to the international standard (1.0). Compared with the data obtained in 2008, there were large declines on the non-cancer risk levels of the heavy metals. This can be especially seen on As, which were as high as 9.1 and 72.4, respectively, for adults and children in 2008. The comparison indicates that the air quality related to elemental pollution in PM$_{2.5}$ have been improved along the 8-year period (from 2008 to 2016) (Liu et al. 2017a). However, in comparison with other Chinese cities, the non-cancer risks were below 1 (0.03 and 0.02 for children and

Fig. 4 Non-cancer (**a**) and cancer risks (**b**) of elements in PM$_{2.5}$ from Xi'an (lines represent the international threshold values for non-cancer and cancer risks, respectively)
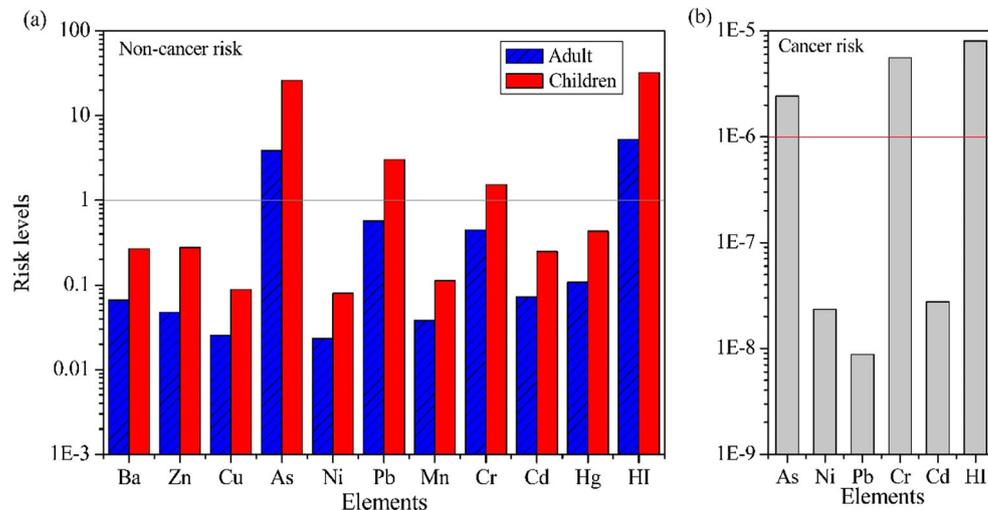
adults) in Nanjing, China, in 2014 (Kong et al. 2015) and were 1.2 and 0.9 in winter and summer of 2010, respectively, in Tianjin, China (Zhang et al. 2015). The values in Xi'an are still much higher than those levels. Such enhanced non-cancer risks demonstrated that it is necessary to have a stricter control of the heavy metal pollutions in this area. Moreover, the hand-mouth ingestion pathway resulted in the higher non-cancer risk and caused higher toxic impacts to the human body. The local authorities should be aware of this kind of exposure pathway by public education.

Figure 4 also shows the cancer risks (ILCR) for the toxic elements in $PM_{2.5}$ in Xi'an. The average ILCR value was 8.0×10^{-6}, far higher than 1×10^{-6} (an international threshold), indicating that these elements had potential cancer risks in general. The values of Ni, Pb, and Cd were well below the guidelines, which can be considered as no obvious cancer risk. The ILCR values of As and Cr were 2.4×10^{-6} and 5.5×10^{-6}, which were higher than the threshold even though slight declines were exhibited compared with those values in 2008 (3.5×10^{-6} and 5.7×10^{-6}, respectively) (Liu et al. 2017a). In addition, our values are at least three magnitudes higher than the ILCR for As, Cd, and Cr of 2.25×10^{-9}, 2.09×10^{-12} and 2.05×10^{-11}, respectively, measured in Tehran, Iran, in 2016 (Mohsenibandpi et al. 2018), and for As, Ni, Pb, and Cd of 3.5×10^{-6}, 5.9×10^{-7}, 2.5×10^{-7}, and 1.4×10^{-7}, respectively, in Malaysia in 2014 (Khan et al. 2016). The reductions on the cancer risks in Xi'an were shown in recent years; however, they are still retained in alert levels. In conclusion, As and Cr in $PM_{2.5}$ had both non-cancer and cancer risks for humans. Their health impacts and controls should be particularly addressed in the study area.

Conclusions

A total of 10 elements (i.e., Ba, Zn, Cu As, Ni, Pb, Mn, Cr, Cd, and Hg) in $PM_{2.5}$ in Xi'an were investigated from May 2015 to April 2016. The annual average value of $PM_{2.5}$ was 62.1 μg m^{-3}, nearly twice of the annual average national standard of 35 μg m^{-3}. The average concentrations of total quantified elements had the lowest value of 413.0 ng m^{-3} in October 2015 and the highest of 6973.8 ng m^{-3} in February 2016. The concentrations of Zn and Ba showed large variations among the sampling period and totally accounted for more than 80% of the total quantified element concentration in both seasons. EFs of Zn, As, Pb, Cd, and Hg exceeded 100, strongly affected by human activities. The results from correlation analysis and PCA model show that coal and other fuel combustion, vehicle exhaust, and industrial activities are the top three pollution sources of $PM_{2.5}$-bounded heavy metals in Xi'an. Health risk assessments demonstrate that the hand-mouth ingestion posed higher health risks than dermal contact

and respiratory inhalation for both children and adults. Many of the elements showed excessive non-carcinogenic and carcinogenic risks in this study. In particular, As and Cr had both kinds of health risks to humans. The results of this study are useful for further researches of $PM_{2.5}$ pollution in Xi'an, providing a reference for source apportionment and emphasizing the importance of air pollution control to improve the air quality and reduce health risks in the polluted northwestern cities of China.

References

Adachi K, Tainosho Y (2004) Characterization of heavy metal particles embedded in tire dust. Environ Int 30(8):1009–1017

Air Quality Guidelines, Particulate matter, ozone, nitrogen dioxide and sulfur dioxide (2006) World Health Organization. WHO press. Geneva

Ajmone MF, Biasioli M, Kralj T, Grčman H, Davidson CM, Hursthouse AS, Madrid L, Rodrigues S (2008) Metals in particle–size fractions of the soils of five European cities. Environ Pollut 152:73–81

Ambient air quality standards of the People's Republic of China (GB 3095–2012) (2012) Ministry of Environmental Protection of the People's Republic of China. Beijing

Cao JJ, Shen ZX, Chow JC, Watson JG, Lee SC, Tie XX, Ho KF, Wang GH, Han YM (2012) Winter and summer $PM_{2.5}$ chemical compositions in fourteen Chinese cities. J Air Waste Manage Assoc 62(10): 1214–1226

Charlesworth S, Miguel ED, Ordonez A (2011) A review of the distribution of particulate trace elements in urban terrestrial environments and its application to considerations of risk. Environ Geochem Health 33:103–123

Chen SH, Sun TH, Zhou QX, Wu GP (2002) Interaction between microorganisms and heavy metals and its application. Chin J Appl Ecol 13(2):239–242 (in Chinese with English abstract)

Chen H, Lu XW, Chang YY, Xue WZ (2014) Heavy metal contamination in dust from kindergartens and elementary schools in Xi'an, China. Environ Earth Sci 71:2701–2709

Chen PF, Bi XH, Zhang JQ, Wu JH, Feng YC (2015) Assessment of heavy metal pollution characteristics and human health risk of exposure to ambient $PM_{2.5}$ in Tianjin, China. Particuology 20:104–109

Deng FL (2008) Analysis on the change of precipitation in Xi'an in the last 57 years. Shaanxi Meteorology 4:21–23 (in Chinese)

Du JH, Zhang YS, He LY (2012) Pollution characteristics and health risk assessment of heavy metals in Shenzhen atmospheric $PM_{2.5}$. J Environ Health 29(9):838–840 (in Chinese)

Fang GC, Huang YL, Huang JH (2010) Study of atmospheric metallic elements pollution in Asia during 2000–2007. J Hazard Mater 180: 115–121

Ferreira BL, De ME (2005) Geochemistry and risk assessment of street dust in Luanda, Angola: a tropical urban environment. Atmos Environ 39:4501–4512

General Administration of Quality Supervision Inspection and Quarantine of the People's Republic of China. Reference Material Certificate, Soil composition analysis standard material (GBW07401–GBW07408) (2003) Geophysical and Geochemical Exploration Research Institute: Langfang, China

Han Y, Du P, Cao J, Posmentier ES (2006) Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, Central China. Sci Total Environ 355:176–186

He GX, Feng H, Zhang HR (2014) The diffusion and attenuation model of $PM_{2.5}$ pollution in air. Mathematics Practice Theory 455:107–118

Hu X, Zhang Y, Ding ZH, Wang TJ, Lian HZ, Sun YY, Wu JC (2012) Bio-accessibility and health risk of arsenic and heavy metals (Cd, Co, Cr, Cu, Ni, Pb, Zn and Mn) in TSP and $PM_{2.5}$ in Nanjing, China. Atmos Environ 57:146–152

Hu CW, Chao MR, Wu KY (2003) Characterization of multiple airborne particulate metals in the surroundings of a municipal waste incinerator in Taiwan. Atmos Environ 37(20):2845–2552

Jiao L, Shen JD, Yao L, Yang L (2013) Pollution characteristics and sources of heavy metals in atmospheric dust fall of Hangzhou. Environ Pollution Control 35(1):73–76 (in Chinese with English abstract)

Jodeh S, Hasan AR, Amarah J, Judeh F, Salghi R, Lgaz H, Jodeh W (2018) Indoor and outdoor air quality analysis for the city of Nablus in Palestine: seasonal trends of PM_{10}, $PM_{5.0}$, $PM_{2.5}$, and $PM_{1.0}$ of residential homes. Air Quality, Atmosphere Health 11:229–237

Kan HD, Chen RJ, Tong SL (2012) Ambient air pollution, climate change, and population health in China. Environ Int 42(1):10–19

Kong SF, Lu B, Ji YQ, Zhao XY, Bai ZP, Xu YH, Liu Y, Jiang H (2012) Risk assessment of heavy metals in road and soil dusts within $PM_{2.5}$, PM_{10} and PM_{100} fractions in Dongying city, Shandong Province, China. J Environ Monit 14:791–803

Kong SF, Ji YQ, Lu B, Chen L, Han B, Li ZY, Bai ZP (2011) Characterization of PM_{10} source profiles for fugitive dust in Fushun—a city famous for coal. Atmos Environ 45:5351–5365

Kong SF, Li L, Li XX, Yin Y, Chen K, Liu DT, Yuan L, Zhang YJ, Shan YP, Ji YQ (2015) The impacts of firework burning at the Chinese Spring Festival on air quality: insights of tracers, source evolution and aging processes. Atmos Chem Phys 15:2167–2184

Khan MF, Hwa SW, Hou LC, Mustaffa NLH, Amil N, Mohamad N, Sahani M, Jaafar SA, Nadzir MSM, Latif MT (2017) Influences of inorganic and polycyclic aromatic hydrocarbons on the sources of $PM_{2.5}$ in the Southeast Asian urban sites. Air Quality, Atmosphere Health 10(8):999–1013

Khan MF, Latif MT, Saw WH, Amil N, Nadzir MSM, Sahani M, Tahir NM, Chung JX (2016) Fine particulate matter in the tropical environment: monsoonal effects, source apportionment, and health risk assessment. Atmospheric Chemistry Physics 16(2):597–617

Lee H, Allen HC (2012) Analytical measurements of atmospheric urban aerosol. Anal Chem 84(3):1196–1201

Lin XH, Zhao Y, Fan XJ, Hu GR, Yu RL (2016) Enrichment characteristics and sources analysis of metal elements in $PM_{2.5}$ in autumn in Nanchang city. Environ Sci 37(1):35–40

Liu R, Zhang H, Gou X, Luo XQ, Yang HY (2014) Approaches of health risk assessment for heavy metals applied in China and advance in exposure assessment models: a review. Ecology Environ Sci 23:1239–1244

Liu PP, Lei YL, Ren HR, Gao JJ, Xu HM, Shen ZX, Zhang Q, Zheng CL, Liu HX, Zhang RJ, Pan H (2017a) Seasonal variation and health risk assessment of heavy metals in $PM_{2.5}$ during winter and summer over Xi'an, China. Atmosphere 8(6):91

Liu XH, Guo JE, Ma LG, Su B, Zhao HF, Lu JM, Lu Q (2017b) Analysis on source of heavy metal elements in $PM_{2.5}$, Taiyuan city 2016. Prev Med Tribune 23(8):564–567

Lu XW, Li LY, Wang LJ, Lei K, Huang J, Zhai YX (2009) Contamination assessment of mercury and arsenic in roadway dust from Baoji, China. Atmos Environ 43:2489–2496

Manalis N, Grivas G, Protonotarios V, Moutsatsou A, Samara C, Chaloulakou A (2005) Toxic metal content of particulate matter (PM_{10}), within the Greater Area of Athens. Chemosphere 60(4):557–566

Meng YT, Zhang YM, Li M (2009) Biogenic Mn oxides for effective desorption of Cd from aquatic environment. Environ Pollut 157:2577–2583

Mohsenibandpi A, Eslami A, Ghaderpoori M, Shahsavani A, Jeihooni AK, Ghaderpoury A, Alinejad A (2018) Health risk assessment of heavy metals on $PM_{2.5}$ in Tehran air, Iran. Data Brief 17:347–355

National Bureau of Statistics of the People's Republic of China (2017) China Statistical Yearbook, 2016, China Statistics Press: Beijing, China

Okuda TK, Masayuki N, Daisuke N (2008) Trends in hazardous trace metal concentrations in aerosols collected in Beijing, China from 2001 to 2006. Chemosphere 72(6):917–924

Oliva SR, Espinosa AJF (2007) Monitoring of heavy metals in top soils, atmospheric particles and plant leaves to identify possible contamination sources. Microchem J 86(1):131–139

Qiu ZW, Xu XQ, Liu WY, Li XX (2018) Investigation into pedestrian exposure to traffic PM around grade separations: a case study in Xi'an, China. Air Quality, Atmosphere & Health PP 1–13

Rastogi N, Singh A, Singh D, Sarin MM (2014) Chemical characteristics of $PM_{2.5}$ at a source region of biomass burning emissions: evidence for secondary aerosol formation. Environ Pollut 184(1):563–569

Shen ZX, Zhang Q, Cao JJ, Zhang LM, Lei YL, Huang Y, Huang RJ, Gao JJ, Zhao ZZ, Zhu CS, Yin XL, Zheng CL, Xu HM, Liu SX (2017) Optical properties and possible sources of brown carbon in $PM_{2.5}$ over Xi'an, China. Atmos Environ 150:322–330

Taylor SR, Mclennan SM (1995) The continental crust: its composition and evolution. An examination of the geochemical record preserved in sedimentary rocks, Blackwell Scientific Publications: Boston

Tokalioglu S, Kartal S (2006) Multivariate analysis of the data and speciation of heavy metals in street dust samples from the Organized Industrial District in Kayseri (Turkey). Atmos Environ 40:2797–2805

USEPA (1989) Risk Assessment Guidance for Superfund. Part A, Human Health Evaluation Manual. Part E, Supplemental Guidance for Dermal Risk Assessment, Part F, Supplemental Guidance for Inhalation Risk Assessment. Available on–line at, https://www.epa.gov/risk/risk–assessment–guidance–superfund–rags–part

USEPA (1996) Soil screening guidance: technical background document. In: Office of soild waste and emergency response, Washington, DC

USEPA (2001) Supplemental guidance for developing soil screening levels for superfund sites. In: Office of soild waste and emergency response, Washington, DC

USEPA (2007) Framework for metals risk assessment. In: Office of Soild Waste and Emergency Response. USA, Washington, DC

USEPA (2011) Exposure Factors Handbook: 2011 Edition. USA Office of Research and Development, Washington, DC 20460

Vallius M, Janssen NAH, Heinrich J, Hoek G, Ruuskanen J (2005) Source and elemental composition of $PM_{2.5}$ in three European cities. Sci Total Environ 337:147–162

Wang P, Cao JJ, Shen ZX, Han YM, Lee SC, Huang Y, Zhu CS, Wang QY, Xu HM, Huang RJ (2015) Spatial and seasonal variations of $PM_{2.5}$ mass and species during 2010 in Xi'an, China. Sci Total Environ 508:477–487

Wang Y, Zhuang GS, Tang AH, Hui Y, Sun YL, Chen S, Zheng AH (2005) The ion chemistry and the source of $PM_{2.5}$ aerosol in Beijing. Atmos Environ 39(21):3771–3784

Wang J, Hu ZM, Chen YY (2013) Contamination characteristics and possible sources of PM_{10} and $PM_{2.5}$ in different functional areas of Shanghai, China. Atmos Environ 68:221–229

Wei BG, Yang LS (2010) A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. Microchem J 94:99–107

Witkowska A, Lewandowska AU, Saniewska D, Falkowska LM (2016) Effect of agriculture and vegetation on carbonaceous aerosol concentrations (PM$_{2.5}$ and PM$_{10}$) in Puszcza Borecka National Nature Reserve (Poland). Air Quality, Atmosphere Health 9(7):761–773

Xu HM, Ho SSH, Cao JJ, Guinot B, Kan HD, Shen ZX, Ho KF, Liu SX, Zhao ZZ, Li JJ, Zhang NN, Zhu CS, Qian Z, Huang RJ (2017) A 10-year observation of PM$_{2.5}$-bound nickel in Xi'an, China: effects of source control on its trend and associated health risks. Sci Rep 7: 41132

Xu Y, Ying Q, Hu JL, Gao Y, Yang Y, Wang DX, Zhang HL (2018) Spatial and temporal variations in criteria air pollutants in three typical terrain regions in Shaanxi, China, during 2015. Air Quality Atmosphere Health 11(1):95–109

Zhang M, Wang H (2009) Concentrations and chemical forms of potentially toxic metals in road–deposited sediments from different zones of Hangzhou, China. J Environ Sci 21(5):625–631

Zhang N, Han B, He F, Xu J, Niu C, Zhou J, Kong SF, Bai ZP (2015) Characterization, health risk of heavy metals, and source apportionment of atmospheric PM$_{2.5}$ to children in summer and winter: an exposure panel study in Tianjin, China. Air Quality, Atmosphere Health 8:347–357

Zhen XR (2015) Analysis on the cause of a continuous pollution process in Shanghai in spring. Shanghai urban environmental and meteorological center, Shanghai.

Zheng N, Liu JS, Wang QC, Liang ZZ (2010) Health risk assessment of heavy metal exposure to street dust in the zinc smelting district, Northeast of China. Sci Total Environ 408:726–733

Zheng XY, Liu XD, Zhao FH, Duan FK, Yu T, Cachier H (2005) Seasonal characteristics of biomass combustion and emission contribution to atmospheric particulates in Beijing. Science China 35(4):346–352 (in Chinese with English abstract)