Aerosol Science and Engineering (2018) 2:1–10
https://doi.org/10.1007/s41810-017-0018-9

ORIGINAL PAPER

Levels, Sources, Markers and Health Risks of Heavy Metals in $PM_{2.5}$ Over a Typical Mining and Metallurgical City of Central China

Jingru Zheng[1,2] · Changlin Zhan[1,2] · Ruizhen Yao[1,2] · Jiaquan Zhang[1,2] · Hongxia Liu[1,2] · Ting Liu[1,2] · Wensheng Xiao[1,2] · Xianli Liu[1,2] · Junji Cao[3]

Received: 24 September 2017 / Revised: 20 November 2017 / Accepted: 29 November 2017 / Published online: 5 December 2017

Abstract
To investigate the pollution characteristics, sources and health risk assessment of various elements in $PM_{2.5}$ of Huangshi city, 54 samples were collected from March 2012 to February 2013. The composition and characteristic of sixteen elements (Mg, Al, Ca, Ti, Cr, Mn, Cu, Zn, V, Fe, As, Pb, Cd, Co, Ni and W) were analyzed by high-sensitivity X-ray fluorescence (XRF). The result showed that the annual mean concentration of $PM_{2.5}$ was 104.4 μg/m^3, far exceeding the secondary level of Ambient Air Quality Standard of China (annual average limit 35 μg/m^3). Element W has the highest annual concentration, followed by Zn, Pb and As. Compared with the concentration limit of National Ambient Air Quality Standard of China, Cd and As in Huangshi were 4.3 times and 32.8 times higher, respectively, than national standard. The concentration of most elements has distinct seasonal characteristic which is higher in winter and lower in summer. Enrichment factor (EF) analysis indicates that W, Fe, Cd, As, Pb, Zn, Cu, Cr, Co and Ni are extremely enriched in $PM_{2.5}$, Ca, Mg and Mn are highly enriched, and V is significant enriched. EF of Ti is less than 2, suggesting minimal pollution. Positive matrix factorization (PMF) analysis indicates that Ca, Ti and Al are associated with fugitive dust, and As is associated with coal-fired industrial activity. W, Cr, Cd, V and Ni are originated from chemical and metallurgical industry activities. Pb, Zn, Cu and Mg are derived from vehicle emissions. The results of the human health risk assessment model show that As may pose great non-carcinogenic risk to children and adults. Cr and As have a higher carcinogenic risk for adults, and Cr has a higher carcinogenic risk for children, and other toxic metals are in relatively safe range.

Keywords Huangshi city · $PM_{2.5}$ · Elements · Enrichment factor · Source · Health risk

1 Introduction

Atmospheric particulates, especially fine particles ($PM_{2.5}$), can diffuse and absorb solar radiation and directly affect visibility and climate change (Booth et al. 2012; Cao et al. 2012b; Pöschl 2005; Ramanathan et al. 2001). Epidemiological studies have confirmed that cardiovascular morbidity and mortality are closely related to atmospheric particulate concentrations (Brook et al. 2010; Pope et al. 2002, 2009; Thurston et al. 2016). Atmospheric particulate matter (PM) is important carrier of toxic and harmful metal elements (such as Cr, As, Cd, Ni, Cu, Pb, Zn, etc.) and other organic pollutants (such as PAHs, VOCs). Studies show that smaller particle, due to its relative larger surface area, carries pollutants that are higher in quantity and complexity and obtains easier access to body's respiratory system and blood circulation, thus impacting human health (Meng et al. 2013); consequently, $PM_{2.5}$ has become a heated topic for current international atmospheric environment.

Many previous studies have analyzed the pollution characteristics, specific sources and toxicity of heavy metals in ambient PM, due to their adverse health effects (Chen et al. 2015; Satsangi et al. 2014; Schleicher et al. 2011; Tecer et al. 2012; Wild et al. 2009). Heavy metals, mostly from traffic and industrial emissions, are differed widely from the sites of ambient environment. Industrial activities such as

✉ Changlin Zhan
chl_zhan@126.com

1 School of Environmental Science and Engineering, Hubei Polytechnic University, Huangshi 435003, China

2 Hubei Key Laboratory of Mine Environmental Pollution Control and Remediation, Huangshi 435003, China

3 Key Laboratory of Aerosol Chemistry and Physics (KLACP), Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710061, China

metallurgical (steel, copper, stainless steel and other forms of nonferrous metals), concrete, ceramic and petrochemical industries have different characteristics of marker elements. For example, metallurgy production emissions are linked to high levels of Cr, Ni, Cu, Zn, Mn, Cd, As, Pb and Sn, while high levels of Ni and V are always regarded as the tracers of petrochemical industries or fuel–oil combustion (Querol et al. 2007). Marker elements may provide certain insights in the interpretation of PM emission sources in receptor-modeling studies.

With the rapid development of China's economy and technology, the problem of urban air pollution has become more complicated and poses a great threat to human health. In 2013, *The 2010 Global Disease Burden Assessment* noted that in 2010, China's outdoor $PM_{2.5}$ pollution resulted in 1.234 million deaths and 25 million years of health life loss in China (Yang et al. 2013). At present, domestic research on atmospheric $PM_{2.5}$ pollution is mainly focused on large cities such as Beijing, Shanghai, Guangzhou, Chengdu, Xi'an, Nanjing, Tianjin, etc., discussing the $PM_{2.5}$ pollution characteristics, element composition, source apportionment and health risk (Cao et al. 2012a; Hu et al. 2012; Huang et al. 2014; Tao et al. 2013; Wang et al. 2006, 2013; Zhang and Cao 2015; Zheng et al. 2005). In recent years, haze events frequently occur over the Wuhan city cluster and its surrounding areas during autumn and winter, and have aroused widespread concern of the public. Unfortunately, study of urban atmospheric $PM_{2.5}$ in central China is rarely reported at present (Guo et al. 2015; Lyu et al. 2016; Wei et al. 1999).

Huangshi City is located in the southeastern part of Hubei Province, at the south bank of the middle reaches of the Yangtze River. It is the suburban center of Wuhan city cluster and is also an important industrial base of raw materials in central China. Huangshi holds rich mineral resources, with more than 190 deposits of iron, copper and gold, providing favorable conditions for the metallurgical, chemical, building materials industries. However, long periods of mineral resource exploitation and smelting have seriously affected the ecological environment of Huangshi area, and heavy metal pollution is particularly serious (Cai et al. 2015; Du et al. 2015; Gao et al. 2003; Yan et al. 2007; Yu et al. 2005). Additionally in recent years, the number of motor vehicles in Huangshi increased yearly, motor vehicle emissions added serious burden to local air pollution. The study of atmospheric $PM_{2.5}$ in Huangshi area is of great significance to understand the composition, content and source of heavy metals in urban atmosphere, so to protect public health and formulate practical control measures.

In this study, the $PM_{2.5}$ samples were collected at a building rooftop of Hubei Polytechnic University, located in Huangshi, from March 2012 to February 2013. The mass concentrations of $PM_{2.5}$ and 16 elements were analyzed. The element composition and sources were assessed, and the health risks of heavy metal elements were evaluated. We hope this study could provide basic data and reference for Huangshi atmospheric environmental management, pollution prevention and health protection.

2 Materials and Methods

2.1 Sampling and Analysis

The sampling site (30°12′35.47″N,115°01′30.38″E) of this study was located on the rooftop of the Environmental Science and Engineering Institute building (about 16 m above ground and 48 m above sea level) in Hubei Polytechnic University of Huangshi city, close to central China (Fig. 1). No single specific pollution sources were identified near the sampling site.

Fifty-four $PM_{2.5}$ samples were collected from March 31, 2012 to February 24, 2013 with battery-powered mini-volume samplers (Airmetrics, Oregon, USA) operating at a flow rate of 5 L/min. One 24-h $PM_{2.5}$ sample was collected on 47-mm teflon filter (Whatman, England) every 6 day. The sampling was started at 9:00 am to next day at 9:00 am. Before and after sampling, the filters were conditioned at 20 ± 1 °C in relative humidity of 50 ± 2% for 24 h. The filters were then weighed by an electronic microbalance with a detection sensitivity of 1 μg (Mettle M3, Switzerland). The filter samples were stored at − 4 °C until pretreatment.

The mass concentration of $PM_{2.5}$ was determined by gravimetric method. The element compositions were analyzed after being exposed to high-sensitivity X-ray fluorescence (Epsilon 5, Netherlands) under certain conditions (30 °C) for 22 min. Sixteen elements (Ca, Mg, Ti, Al, Cr, Mn, Cu, Zn, V, Fe, As, Pb, Cd, Co, Ni and W) were measured for each $PM_{2.5}$ sample.

2.2 Enrichment Factors (EFs)

EFs are often used to assess the degree of element enrichment in atmospheric particulate matter and determine the geological or anthropogenic origin of a certain pollutant element. The equation for the EFs is:

$$\mathrm{EF} = \frac{(C_i/C_n)_{\mathrm{sample}}}{(C_i/C_n)_{\mathrm{background}}}, \tag{1}$$

where i is the element of interest, C_i is the concentration of i, and C_n is the concentration of a reference element. $(C_i/C_n)_{\mathrm{sample}}$ represents the concentration ratio of studied element collected in $PM_{2.5}$ sample to the reference element, and $(C_i/C_n)_{\mathrm{background}}$ is the concentration ratio of studied element to reference element of background soil. In this study,

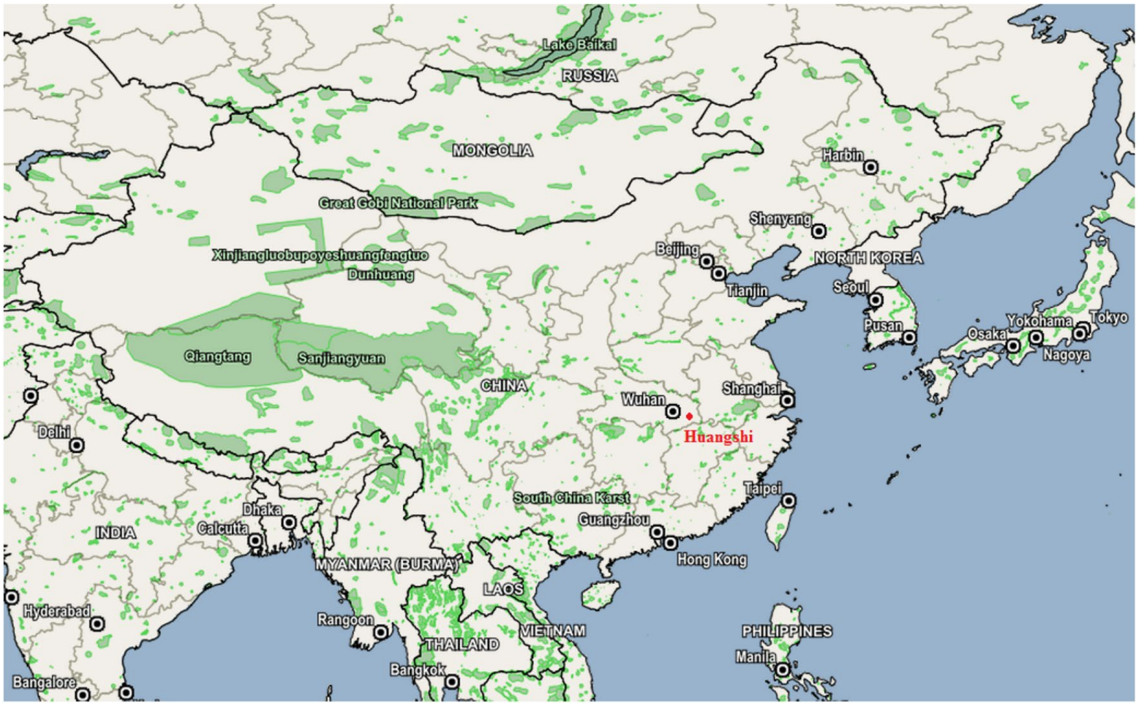

Fig. 1 Location of Huangshi City. The green color in the map means protected areas (color figure online)

aluminum (Al) was chosen as the reference element, and the concentration of Al (7.19%) was taken from soil background values in China (China National Environmental Monitoring Center 1990). If the EFs value is between 0 and 1, it generally indicates that the element is not enriched in the atmosphere, but primarily originated from geological weathering. If the EFs value is between 1 and 10, it means that the element was influenced by both natural and anthropogenic sources. If the EFs is higher than 10, it indicates that the element was dominated by anthropogenic contributions. According to the study of Sutherland (2000), the pollution enrichment levels can be divided into a five-category system: when EFs is less than 2, it suggests nearly no enrichment or minimal pollution; when EFs is between 2 and 5, it suggests moderate enrichment; when EFs is between 5 and 20, it suggests significant enrichment; when EFs is between 20 and 40, it suggests highly enrichment; when EFs is greater than 40, it suggests extremely enrichment.

2.3 Source Apportionment

Positive matrix factorization (PMF) is a multivariate receptor model that estimates the source profiles and their contributions based on a weighted least square approach (Paatero and Tapper 1993). It is also a tool for analyzing atmospheric particulate source recommended by the US Environmental Protection Agency (US EPA) and the Ministry of Environmental Protection of China. In the present study, PMF 5.0 was employed with the inclusion of 16 elements in the model computation.

2.4 Health Risk Assessment

According to the human health risk assessment model based on those developed by the US EPA (2011a), exposure parameters suitable for Chinese were selected, exposure concentration (EC) was estimated to assess the health risks of ten inhalable heavy elements (Cr, Mn, Cu, Zn, V, As, Pb, Cd, Co and Ni) in $PM_{2.5}$. The reference dose of W and Fe was not available, so the assessment of health risks in this study did not include W and Fe. The assessment subjects were divided into two groups: adults (> 15 years) and children (0–15 years), owning to the differences in their behavior and respiratory system (Li et al. 2016). In this study, Mn, Cu, Zn and V are non-carcinogenic, and Cr, As, Cd, Co, Pb and Ni are carcinogenic.

The average daily dose of heavy metals exposure through inhalation of particulate matter is calculated by following the Eq. (2):

$$\mathrm{EC_{inh}} = \frac{C \times \mathrm{ET} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{AT}}, \tag{2}$$

where C represents heavy metal concentration in $PM_{2.5}$ (μg/m^3); ET is exposure time (h/day); EF is exposure frequency (day/year); ED is duration of exposure (a); and AT is the average exposure time through inhalation (h). For non-carcinogens, AT = ED × 365 days × 24 h/day; for carcinogens, AT = 70 × 365 days × 24 h/day. The parameters involved in the model are shown in Table 1.

The risk of exposure to heavy metals through inhalation is calculated by Eqs. (3) and (4) (Li et al. 2016; You et al. 2017):

$$\mathrm{HQ} = \frac{\mathrm{EC_{inh}}}{\mathrm{Rf}C_i \times 1000}, \quad (3)$$

$$\mathrm{ELCR} = \mathrm{IUR} \times \mathrm{EC_{inh}}, \quad (4)$$

where HQ is non-carcinogenic quotient; ELCR is excess lifetime carcinogenic risk; $\mathrm{Rf}C_i$ is the inhalation reference concentration, mg/m^3; IUR is the inhalation unit risk, per μg/m^3.

3 Results and Discussion

3.1 Mass Concentrations and Characteristics of $PM_{2.5}$ and Elements

Table 2 shows the mass concentrations of atmospheric $PM_{2.5}$ and 16 elements in Huangshi. The results indicate that during the sampling period, the average annual $PM_{2.5}$ concentration in Huangshi is 104.4 μg/m^3, and the mean values of $PM_{2.5}$ in spring, summer, autumn and winter are (96.9 ± 27.0) μg/m^3, (60.7 ± 24.7) μg/m^3, (111.1 ± 45.8) μg/m^3 and (114.0 ± 43.8) μg/m^3, respectively. Compared with the average 24-h (75 μg/m^3) $PM_{2.5}$ mass concentration standard set from China's "Environmental Quality Standards" (GB 3095-2012 2012), except for summer, Huangshi $PM_{2.5}$ concentration in spring, autumn and winter is 1.29 times, 1.48 times and 1.52 times higher than national average, respectively. The concentration of $PM_{2.5}$ in autumn and winter is evidently higher than that in summer, which is similar to many other studies. The main reason is that

Table 1 Exposure parameters via respiration

Item	Adults	Children	References
EF/day/a	350	350	(HJ 25.3-2014 2014)
ED/a	24	6	(HJ 25.3-2014 2014)
AT (carcinogenic)/h	70 × 365 × 24	70 × 365 × 24	(US EPA 2013)
AT (non-carcinogenic)/h	ED × 365 × 24	ED × 365 × 24	(US EPA 2013)

Table 2 $PM_{2.5}$ (μg/m^3) and 16 metal elements (ng/m^3) mass concentrations in Huangshi city

Component	Range	Spring		Summer		Autumn		Winter		Annual average
		Average	SD	Average	SD	Average	SD	Average	SD	
$PM_{2.5}$	29.4–501.4	96.9	27.0	60.7	24.7	111.1	45.8	114.0	43.8	104.4
Ca	13.5–1846.6	447.4	264.8	356.2	135.2	506.1	445.2	508.1	514.1	455.0
Mg	0–656.7	239.2	124.2	234.2	194.1	253.1	212.8	277.8	171.2	251.9
Ti	0–101.4	24.2	18.5	14.4	8.0	29.1	22.8	30.7	26.9	24.6
Al	107.9–1337.1	401.1	223.5	275.0	107.9	404.4	287.4	449.4	335.1	381.1
Cr	8.9–111.9	33.5	16.8	23.6	17.0	32.0	25.7	36.1	24.0	31.1
Mn	0.7–158.6	61.5	33.0	28.2	17.6	51.5	37.6	68.6	34.9	51.8
Fe	73.6–1748.4	847.8	341.1	424.4	166.0	776.3	455.9	811.8	396.3	705.6
Cu	11.0–484.9	50.1	32.8	26.5	13.2	78.7	117.0	52.0	26.3	51.9
Zn	28.2–2045.7	580.3	353.0	403.3	466.1	663.8	391.2	478.8	280.8	528.1
As	0–1550.7	223.2	271.4	156.7	389.3	241.1	369.2	320.4	119.1	196.9
Pb	28.4–1225.3	370.5	301.6	218.7	293.7	332.0	268.0	272.5	160.0	293.3
Cd	0–57.6	14.7	13.8	17.5	15.7	32.5	12.7	19.1	8.7	21.4
W	46.7–5602.2	2601.9	996.1	2402.0	78.6	2286.5	46.7	2170.0	132.6	2348.1
Co	0–8.4	4.1	3.0	2.1	1.7	3.1	2.5	2.7	1.9	2.9
Ni	0–19.3	6.3	3.0	5.3	2.8	6.3	3.0	6.5	4.4	6.1
V	0–6.8	2.2	2.3	2.6	1.7	1.8	2.0	1.6	2.1	2.1

SD standard deviation

solar radiation is relatively weak during autumn and winter in Huangshi when the atmospheric boundary layer is low, the pollutants are difficult to disperse, and less rainfall also contributes to the accumulation of pollutants. While during summer, solar radiation is stronger and boundary layer is higher, assisted by frequent rainfall removing pollutants, $PM_{2.5}$ concentration could remain at a lower level. Comparing with other cities, annual average of $PM_{2.5}$ mass concentration in Huangshi is similar to that of Beijing (101 μg/m^3, Zheng et al. 2005), Shanghai (103.07 μg/m^3, Wang et al. 2013) and Shijiazhuang (101.4 μg/m^3, Wang et al. 2013), however, significantly higher than that of Xiamen (34.1 μg/m^3, Zhang and Cao 2015), Shenzhen (32.0 μg/m^3, Zhang and Cao 2015), Chongqing (59.1 μg/m^3, Zhang and Cao 2015), and other cities in Europe or North America (Cheng et al. 2016; Salameh et al. 2015).

Element W has the highest concentration in $PM_{2.5}$ of Huangshi (2348.1 ng/m^3). W is a rare metal element, commonly used for special alloy steel, which are massively produced for cutting tools and mining tools. Tungsten ore reserves are abundant in Huangshi, together with enterprises of special steel production and processing, resulted in the high enrichment of W in $PM_{2.5}$ of this region. While no similar report is found in studies of other cities. The order of mass concentration of studied element is W > Fe > Zn > Ca > Al > Pb > As > Cu > Mn > Cr > Ti > Cd > Ni > Co > V. Among them, the average concentration of Pb, Cd and As is 293.3, 21.4 and 196.9 ng/m^3, respectively, which is 0.6 times, 4.3 times and 32.8 times of the reference concentration limit in the Ambient Air Quality Standard of China (GB 3095-2012 2012). Element As exceeds the limit drastically. V has the lowest annual average concentration (2.1 ng/m^3), well below the reference concentration of WHO (1000 ng/m^3). The average annual concentrations of Zn, Cu, Mn, Cr, Ni and Co are 582.1, 51.9, 51.8, 31.1, 6.1 and 2.9 ng/m^3, respectively; however, the current Ambient Air Quality Standard of China (GB 3095-2012 2012) has no concentration limits requirement for these elements.

Regard to seasonal variation, the mass concentrations of Ca, Mg, Ti, Al, Cr, Mn, As and Ni all show the highest concentration in winter and the lowest concentration in summer, which is consistent with the variation of $PM_{2.5}$ mass concentration. The seasonal variations of Fe, Cu, Zn and Pb are similar, which is high in spring, autumn and winter, while lower in summer. Mass concentration of V is highest in summer and lowest in winter, while Cd concentration is highest in autumn and lowest in spring. W mass concentration shows a trend of spring > summer > autumn > winter. The possible reasons for most of the metal element concentrations being lowest in summer are: (1) high frequent precipitation in summer enhances wet deposition effect; (2) the surface runoff formed by the summer rainfall to certain extent suppress fugitive dust caused by city traffic, and reduce their contribution to atmospheric particulate; (3) flourishing vegetation in summer absorbs and removes some heavy metals from the atmosphere. The seasonal variation of particular elements may be related to specific pollution sources in the region, which remains to be further studied.

As shown in Table 3, $PM_{2.5}$ metal element concentrations in China's large- and medium-sized cities are significantly higher than those of overseas, indicating that domestic urban air pollution of metal elements is more severe and lead to greater damage to human health. Because of the differences in sampling time, sampling season, type of sampling site, analysis method and emission source in different cities, there are big differences in the concentration of metal elements in $PM_{2.5}$ in different cities at home and abroad.

3.2 EF Characteristics and Source of Elements

3.2.1 EF

The annual EF for 16 elements is shown in Fig. 2. It is clear that the EF value of W is the highest, nearly reaching 277853.2; followed by Fe and Cd, which exceed 10,000; Zn, As, Pb and Cu also show high EF (> 100); Ca, Cr, Co, Mn and Ni appear to be greater than 10. It suggests that these extremely enriched elements were probably largely affected by anthropogenic emissions, in consistent with the highly industrialized environment studied. W is possibly related to the prosperous special steel industry, while Fe and Cd are more likely impacted by the industrial processes of iron and steel smelting. The enrichment of Ca may be related to cement production and construction fugitive dust. The EF values of Mg and V are 7.4 and 4.3, respectively, which suggests that they were influenced both by natural and anthropogenic sources. Ti has an EF of 0.9, mainly originating from natural sources such as crust or rock weathering.

The order of the mean annual EF value of element in Huangshi city is: W > Fe > Cd > As > Pb > Zn > Cu > Cr > Co > Ni > Ca > Mn > Mg > V > Ti, which also shows their accumulation degree. According to the Sutherland classification of enrichment factor (Sutherland 2000), the mean value EF of W, Fe, Cd, As, Pb, Zn, Cu, Cr, Co and Ni is greater than 40, indicating that these elements are super-enriched and critically harmful. The EF of Ca, Mg and Mn is between 5 and 20, indicating significant enrichment, and the EF value of V is between 2 and 5, which is moderate enrichment. The EF value of Ti is less than 2, generally no enrichment.

3.2.2 PMF Fingerprints

The source apportionment of 16 elements in $PM_{2.5}$ is determined by PMF source analysis method. After several times of operation, analysis and comparison, four factors were

Table 3 Element concentration (ng/m^3) in $PM_{2.5}$ in Huangshi comparison with other cities

City	Sampling time	Ca	Mg	Ti	Al	Cr	Mn	Fe	Cu	Zn	As	Pb	Cd	W	Co	Ni	V	References
Huangshi, China	2012.3–2013.2	455.0	251.9	24.6	381.1	31.1	51.8	705.6	51.9	528.1	196.9	293.3	21.4	2348.1	2.9	6.1	2.1	This study
Chengdu, China	2011	402	196	50	560	9.2	66	693	23	350	20	172	3.5	–	–	2.5	1.7	Tao et al. (2014)
Beijing, China	2005.3–2006.2	900	290	80	790	50	90	1130	70	530	20	240	50	–	–	20	30	Yang et al. (2011)
Foshan, China	2008 winter	–	–	–	–	–	200.6	–	283.8	2214	76.6	675.7	42.6	–	–	–	40	Tan et al. (2014)
Xinxiang, China	2014.1–2014.2	6380	1220	340	3260	140	90	1500	50	640	100	400	20	–	3	70	130	Feng et al. (2016)
Sydney, Australia	2001.1–2011.12	16	–	3	19	0.5	1	27	2	6	–	5	–	–	–	0.4	0.3	Cohen et al. (2012)
Phoenix, USA	2001.4–2003.10	240	–	20	–	–	4.7	290	6.4	12	0.6	3	–	–	–	0.3	3	Brown et al. (2007)
Izmir, Turkey	2004.6–2005.5	1660.5	101.2	–	834.2	24.0	16.1	393.4	35.8	176.9	–	92.3	1.2	–	–	15.7	12.3	Yatkin and Bayram (2008)

extracted by the PMF model, and the result of factor profiles is shown in Fig. 3. The extracted factors are interpreted as follows.

Factor 1 has high loadings of Ca, Ti and Al, and explains 66.3, 63.2 and 47.4% of variance, respectively. Ca is a representative indicator of cement dust, mainly from cement and gypsum plants or construction sites (Kim et al. 2004). Ti and Al are important markers of crustal source or soil dust (Lough et al. 2005; Viana et al. 2008). Thus, factor 1 is related to crust dust or soil dust.

Factor 2 explains approximately 89.6% of the variance in As, which has the highest loading. Many previous studies have shown that emissions from coal combustion contains higher concentration of As (Duan and Tan 2013; Kang et al. 2011; Tian et al. 2010). This factor is attributed to emissions from coal combustion.

Factor 3 explains 81.7% of the variance for W. Furthermore, the factor profile is dominated by Ni, V, Cr and Cd, which explains 72.5, 64.2, 54.5 and 53.4% of the variance, respectively. W is mainly used in alloy manufacturing and metal processing (Yih and Wang 1979). In addition to fuel combustion (Vallius et al. 2005), Ni and V could also derive from the mineral extraction process (Brown et al. 2007). Cr and Cd are the symbolic elements (Alleman et al. 2010) in particulate matter which emitted from the petrochemical industry; they also come from the high temperature combustion of coal, oil and garbage (Uberoi and Shadman 1991). Huangshi is an important base for iron ore and nonferrous mineral production in China, many metal manufacturing and processing, metal smelting enterprises. All these industrial activities may have an important contribution to the heavy metal elements, such as W, Ni, V, Cr and Cd in $PM_{2.5}$. Therefore, factor 3 is possibly from anthropogenic source, which is related to the activities of the chemical and metallurgical industries.

In factor 4, the loadings of Pb, Zn, Cu and Mg are higher, which explains 74.2, 69.6, 39.9 and 35.9% of the variance, respectively. Pb and Zn are often used to indicate motor vehicle exhaust (Grieshop et al. 2006; Tecer et al. 2012). The high loading of Cu is a clear marker of vehicles exhaust, tires and brakes abrasion (Kuang et al. 2004), while the presence of Mg could be derived from traffic fugitive dust. Therefore, the origin of this factor is mainly related to traffic exhaust emissions.

3.3 Health Risk Analysis

Carcinogenic risk and non-carcinogenic analysis of 10 toxic heavy metal elements contained in Huangshi $PM_{2.5}$ are shown in Table 4. Element As has the highest non-carcinogenic risk (4.32), significantly higher than the limit of US EPA, indicating that As may lead to non-carcinogenic health risks for both adults and children. The

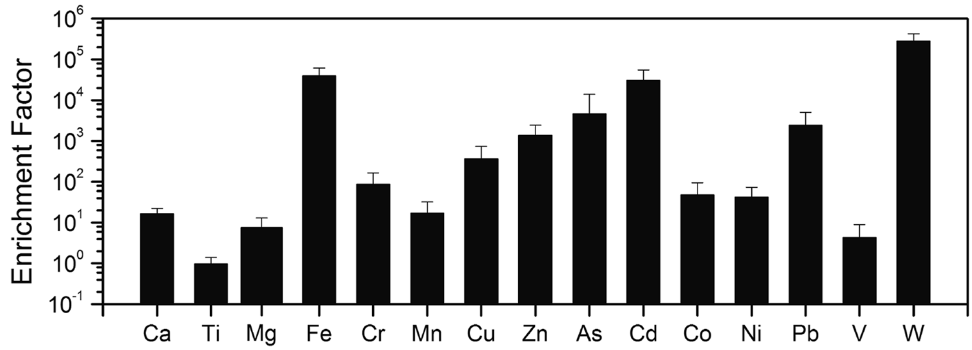

Fig. 2 Enrichment factor (EF) of 16 elements in Huangshi $PM_{2.5}$

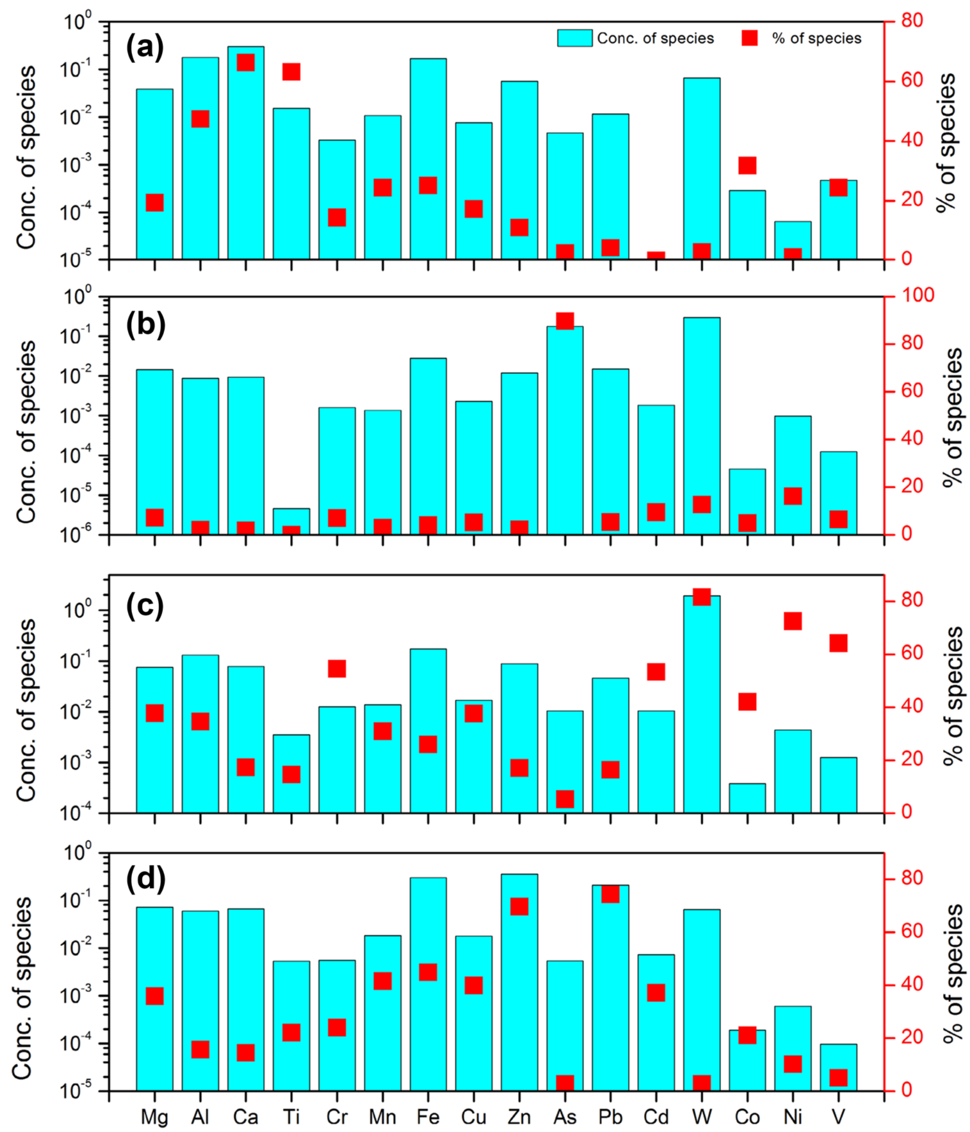

Fig. 3 PMF fingerprints of 16 elements in Huangshi $PM_{2.5}$

non-carcinogenic risk order is As > Mn > Cd > Co > Ni > Cr > V. Li et al. (2016) found that the HQ values of As, Mn and Cd in $PM_{2.5}$ were 3.07, 3.06 and 1.20, respectively, in Chengdu, China, implying a non-carcinogenic risk for both adults and children, which is similar to the order of non-cardiogenic risk value in this study.

As seen from Table 4, the risks of carcinogenic heavy metals for adults and children are similar, both following

Table 4 Cardiogenic risk of inhalable toxic heavy metals in Huangshi $PM_{2.5}$

Element	RfC_i^a	IUR[a]	Non-carcinogenic	Carcinogenic	
				Adult	Children
Pb		8.00E−05		7.71E−06	1.93E−06
V	1.00E−04		2.01E−02		
Mn	5.00E−05		9.94E−01		
Cu					
Zn					
Cr	1.00E−04	8.40E−02	1.02E−01	8.60E−04	2.15E−04
As	1.50E−05	4.30E−03	4.32E+00	2.78E−04	6.96E−05
Cd	1.00E−05	1.80E−03	7.04E−01	1.27E−05	3.17E−06
Co	6.00E−06	9.00E−03	1.60E−01	8.65E−06	2.16E−06
Ni	1.40E−05	2.40E−04	1.43E−01	4.81E−07	1.20E−07

[a] US EPA (2011b)

the descending order of Cr > As > Cd > Co > Pb > Ni. For adults, the carcinogenic risk values for Cr and As were 8.60×10^{-4} and 2.78×10^{-4}, respectively, which exceeded the carcinogenic risk threshold (10^{-6}–10^{-4}); the carcinogenic risk of Cd exceeded 1×10^{-4}, but within the range of cancer risk thresholds. For children, the carcinogenic risk value of Cr is 2.15×10^{-4}, which exceeds the threshold of carcinogenic risk. The carcinogenic risk of As is 6.96×10^{-5}, slightly lower than 1×10^{-4}, which means potential carcinogenic risk for children. The carcinogenic risk of adults with six carcinogenic elements was higher than that of children. The carcinogenic risk found in this study was significantly higher than that in Nanjing (Hu et al. 2012), Chengdu (Li et al. 2016) and Tianjin (Chen et al. 2015), implying greater impact on the public health, the local environmental protection departments should take appropriate measures to reduce its harm.

4 Conclusion

During the period from March 2012 to February 2013, $PM_{2.5}$ samples were collected in Huangshi city, and the concentrations of 16 metal elements were analyzed. The main conclusions were as follows:

1. The annual $PM_{2.5}$ average concentration in Huangshi city is 104.4 μg/m^3, which is significantly higher than that of the national environmental air quality standard, indicating a critical pollution condition. Element W content is highest in $PM_{2.5}$, V concentration the lowest; As and Cd content exceeded the standard by 32.8 times and 4.3 times. Most elements showing seasonal trend of high in winter and low in summer, similar with seasonal variation of $PM_{2.5}$ mass.
2. EF analysis shows that, except Ti, the other 15 elements were all enriched in different degrees. W, Fe, Cd, As, Pb, Zn, Cu, Cr, Co and Ni are extremely enriched, Ca, Mg and Mn are significantly enriched, and V is moderately enriched.
3. PMF source analysis results show that there are four main sources of metal elements in $PM_{2.5}$ of Huangshi area: soil dust or fugitive dust (Ca, Ti, Al), coal combustion (As), chemical industry and metallurgical industry (W, Ti, Ni, V, Cr, Cd), motor vehicle emissions (Pb, Cu, Zn, Mg).
4. The results of health risk assessment showed that the non-carcinogenic risk of element As is higher than 1, indicating a high risk of non-carcinogenesis for adults and children. The carcinogenic risk of Cr and As is higher than the tolerate limit (1×10^{-4}) and may therefore poses a greater risk of cancer in adults. For children, the carcinogenic risk of Cr is higher than the threshold range (10^{-6}–10^{-4}), indicating that there may be a greater risk of cancer.

Acknowledgements This research was supported by the Ministry of Science of Technology (2013FY112700), the College Science Technology Research Project of Hubei Province (Q20134404), the National Natural Science Foundation of China (41603117), the Talent Introduction Projects of Hubei Polytechnic University (16xjz02R) and the Outstanding Youth Science and Technology Innovation Team Projects of Hubei Province (T201729).

References

Alleman LY, Lamaison L, Perdrix E, Robache A, Galloo JC (2010) PM_{10} metal concentrations and source identification using positive matrix factorization and wind sectoring in a French industrial zone. Atmos Res 96(4):612–625

Booth BB, Dunstone NJ, Halloran PR, Andrews T, Bellouin N (2012) Aerosols implicated as a prime driver of twentieth-century North Atlantic climate variability. Nature 484(7393):228–232

Brook RD, Rajagopalan S, Pope CA, Brook JR, Bhatnagar A, Diez-Roux AV, Holguin F, Hong Y, Luepker RV, Mittleman MA, Peters A, Siscovick D, Smith SC, Whitsel L, Kaufman JD (2010) Particulate matter air pollution and cardiovascular disease. Circulation 121(21):2331–2378

Brown SG, Frankel A, Raffuse SM, Roberts PT, Hafner HR, Anderson DJ (2007) Source apportionment of fine particulate matter in Phoenix, AZ, using positive matrix factorization. J Air Waste Manag 57(6):741–752

Cai LM, Xu ZC, Qi JY, Feng ZZ, Xiang TS (2015) Assessment of exposure to heavy metals and health risks among residents near Tonglushan mine in Hubei, China. Chemosphere 127:127–135

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

Cao JJ, Wang QY, Chow JC, Watson JG, Tie XX, Shen ZX, Wang P, An ZS (2012b) Impacts of aerosol compositions on visibility impairment in Xi'an, China. Atmos Environ 59:559–566

Chen P, Bi X, Zhang J, Wu J, Feng Y (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

Cheng Z, Luo L, Wang S, Wang Y, Sharma S, Shimadera H, Wang X, Bressi M, de Miranda RM, Jiang J, Zhou W, Fajardo O, Yan N, Hao J (2016) Status and characteristics of ambient $PM_{2.5}$ pollution in global megacities. Environ Int 89:212–221

China National Environmental Monitoring Center (1990) Soil element background value in China. China Environmental Science Press, Beijing, p 406

Cohen DD, Crawford J, Stelcer E, Atanacio AJ (2012) Application of positive matrix factorization, multi-linear engine and back trajectory techniques to the quantification of coal-fired power station pollution in metropolitan Sydney. Atmos Environ 61:204–211

Du P, Xie Y, Wang S, Zhao H, Zhang Z, Wu B, Li F (2015) Potential sources of and ecological risks from heavy metals in agricultural soils, Daye city, China. Environ Sci Pollut Res 22(5):3498–3507

Duan J, Tan J (2013) Atmospheric heavy metals and arsenic in China: situation, sources and control policies. Atmos Environ 74:93–101

Feng J, Yu H, Liu S, Su X, Li Y, Pan Y, Sun J (2016) PM2.5 levels, chemical composition and health risk assessment in Xinxiang, a seriously air-polluted city in North China. Environ Geochem Health. https://doi.org/10.1007/s10653-10016-19874-10655

Gao Y, He J, Ling W, Hu H, Liu F (2003) Effects of organic acids on copper and cadmium desorption from contaminated soils. Environ Int 29(5):613–618

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

Grieshop AP, Lipsky EM, Pekney NJ, Takahama S, Robinson AL (2006) Fine particle emission factors from vehicles in a highway tunnel: effects of fleet composition and season. Atmos Environ 40:287–298

Guo H, Zhou J, Wang L, Zhou Y, Yuan J, Zhao R (2015) Seasonal variations and sources of carboxylic acids in $PM_{2.5}$ in Wuhan, China. Aerosol Air Qual Res 15:517–528

HJ 25.3-2014 (2014) Technical guidelines for risk assessment of contaminated sites (in Chinese). Ministry of Environmental Protection of the People's Republic of China

Hu X, Zhang Y, Ding Z, Wang T, Lian H, Sun Y, Wu J (2012) Bioaccessibility and health risk of arsenic and heavy metals (Cd Co, Cr, Cu, Ni, Pb, Zn and Mn) in TSP and PM2.5 in Nanjing. China Atmos Environ 57:146–152

Huang RJ, Zhang Y, Bozzetti C, Ho KF, Cao JJ, Han YM, Daellenbach KR, Slowik JG, Platt SM, Canonaco F (2014) High secondary aerosol contribution to particulate pollution during haze events in China. Nature 514(7521):218–222

Kang Y, Liu G, Chou C-L, Wong MH, Zheng L, Ding R (2011) Arsenic in Chinese coals: distribution, modes of occurrence, and environmental effects. Sci Total Environ 412–413:1–13

Kim E, Hopke PK, Edgerton ES (2004) Improving source identification of Atlanta aerosol using temperature resolved carbon fractions in positive matrix factorization. Atmos Environ 38(20):3349–3362

Kuang C, Neumann T, Norra S, Stüben D (2004) Land use-related chemical composition of street sediments in Beijing. Environ Sci Pollut Res Int 11(2):73–83

Li Y, Zhang Z, Liu H, Zhou H, Fan Z, Lin M, Wu D, Xia B (2016) Characteristics, sources and health risk assessment of toxic heavy metals in $PM_{2.5}$ at a megacity of southwest China. Environ Geochem Health 38(2):353–362

Lough GC, Schauer JJ, Park JS, Shafer MM, DeMinter JT, Weinstein JP (2005) Emissions of metals associated with motor vehicle roadways. Environ Sci Technol 39(3):826–836

Lyu X, Chen N, Guo H, Zeng L, Zhang W, Shen F, Quan J, Wang N (2016) Chemical characteristics and causes of airborne particulate pollution in warm seasons in Wuhan, central China. Atmos Chem Phys 16(16):10671–10687

Meng X, Ma Y, Chen R, Zhou Z, Chen B, Kan H (2013) Size-fractionated particle number concentrations and daily mortality in a Chinese city. Environ Health Perspect 121(10):1174–1178

Paatero P, Tapper U (1993) Analysis of different modes of factor analysis as least squares fit problems. Chemometr Intell Lab 18(2):183–194

Pope CA III, Burnett RT, Thun MJ, Calle EE, Krewski D, Ito K, Thurston GD (2002) Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. JAMA 287(9):1132–1141

Pope CA III, Burnett RT, Krewski D, Jerrett M, Shi Y, Calle EE, Thun MJ (2009) Cardiovascular mortality and exposure to airborne fine particulate matter and cigarette smoke. Circulation 120(11):941–948

Pöschl U (2005) Atmospheric aerosols: composition, transformation, climate and health effects. Angew Chem Int Ed 44(46):7520–7540

Querol X, Viana M, Alastuey A, Amato F, Moreno T, Castillo S, Pey J, Rosa J, Campa AS, Artíñano B, Salvador P, Santos SGD, Fernández-Patier R, Moreno-Grau S, Negral L, Minguillón MC, Monfort E, Gil JI, Inza A, Ortega LA, Santamaría JM, Zabalza J (2007) Source origin of trace elements in PM from regional background, urban and industrial sites of Spain. Atmos Environ 41:7219–7231

Ramanathan V, Crutzen P, Kiehl J, Rosenfeld D (2001) Aerosols, climate, and the hydrological cycle. Science 294(5549):2119–2124

Salameh D, Detournay A, Pey J, Pérez N, Liguori F, Saraga D, Bove MC, Brotto P, Cassola F, Massabò D, Latella A, Pillon S, Formenton G, Patti S, Armengaud A, Piga D, Jaffrezo JL, Bartzis J, Tolis E, Prati P, Querol X, Wortham H, Marchand N (2015) $PM_{2.5}$ chemical composition in five European Mediterranean cities: a 1-year study. Atmos Res 155:102–117

Satsangi PG, Yadav S, Pipal AS, Kumbhar N (2014) Characteristics of trace metals infine ($PM_{2.5}$) and inhalable (PM_{10}) particles and its health risk assessment along with in silico approach in indoor environment of India. Atmos Environ 92:384–393

Schleicher NJ, Norra S, Chai F, Chen Y, Wang S, Cen K, Yu Y, Stuben D (2011) Temporal variability of trace metal mobility of urban particulate matter from Beijing—a contribution to health impact assessments of aerosols. Atmos Environ 45:7248–7265

Sutherland RA (2000) A comparison of geochemical information obtained from two fluvial bed sediment fractions. Environ Geol 39(3–4):330–341

Tan JH, Duan JC, Ma YL, Yang FM, Cheng Y, He KB, Yu YC, Wang JW (2014) Source of atmospheric heavy metals in winter in Foshan, China. Sci Total Environ 493:262–270

Tao J, Zhang L, Engling G, Zhang R, Yang Y, Cao J, Zhu C, Wang Q, Luo L (2013) Chemical composition of $PM_{2.5}$ in an urban environment in Chengdu, China: importance of springtime dust storms and biomass burning. Atmos Res 122:270–283

Tao J, Gao J, Zhang L, Zhang R, Che H, Zhang Z, Lin Z, Jing J, Cao J, Hsu SC (2014) $PM_{2.5}$ pollution in a megacity of southwest China: source apportionment and implication. Atmos Chem Phys 14(16):8679–8699

Tecer LH, Tuncel G, Karaca F, Alagha O, Süren P, Zararsız A, Kırmaz R (2012) Metallic composition and source apportionment of fine and coarse particles using positive matrix factorization in the southern Black Sea atmosphere. Atmos Res 118:153–169

Thurston GD, Ahn J, Cromar KR, Shao Y, Reynolds HR, Jerrett M, Lim CC, Shanley R, Park Y, Hayes RB (2016) Ambient particulate matter air pollution exposure and mortality in the NIH-AARP diet and health cohort. Environ Health Perspect 124(4):484–490

Tian HZ, Wang Y, Xue ZG, Cheng K, Qu YP, Chai FH, Hao JM (2010) Trend and characteristics of atmospheric emissions of Hg, As, and Se from coal combustion in China, 1980–2007. Atmos Chem Phys 10(23):11905–11919

Uberoi M, Shadman F (1991) High-temperature removal of cadmium compounds using solid sorbents. Environ Sci Technol 25(7):1285–1289

US EPA (2011a) Risk Assessment Guidance for Superfund. In: Part A: human health evaluation manual; part E, supplemental guidance for dermal risk assessment; part F, supplemental guidance for inhalation risk assessment, vol. I. http://www.epa.gov/oswer/riskassessment/human_health_exposure.htm

US EPA (2011b) The Screening Level (RSL) Tables (Last updated June 2011). http://www.epa.gov/region9/superfund/prg/index.html

US EPA (2013) User's guide/technical background document for US EPA Region 9's RSL tables. Washington, D C, US Environmental Protection Agency. http://www.epa.gov/region9/superfund/prg.htm

Vallius M, Janssen NAH, Heinrich J, Hoek G, Ruuskanen J, Cyrys J, Van Grieken R, de Hartog JJ, Kreyling WG, Pekkanen J (2005) Sources and elemental composition of ambient $PM_{2.5}$ in three European cities. Sci Total Environ 337(1):147–162

Viana M, Kuhlbusch TAJ, Querol X, Alastuey A, Harrison RM, Hopke PK, Winiwarter W, Vallius M, Szidat S, Prévôt ASH, Hueglin C, Bloemen H, Wåhlin P, Vecchi R, Miranda AI, Kasper-Giebl A, Maenhaut W, Hitzenberger R (2008) Source apportionment of particulate matter in Europe: a review of methods and results. J Aerosol Sci 39(10):827–849

Wang X, Bi X, Sheng G, Fu J (2006) Chemical composition and sources of PM_{10} and $PM_{2.5}$ aerosols in Guangzhou, China. Environ Monit Assess 119(1):425–439

Wang J, Hu Z, Chen Y, Chen Z, Xu S (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 F, Teng E, Wu G, Hu W, Wilson W, Chapman R, Pau J, Zhang J (1999) Ambient concentrations and elemental compositions of PM_{10} and $PM_{2.5}$ in four Chinese cities. Environ Sci Technol 33(23):4188–4193

Wild P, Bourgkard E, Paris C (2009) Lung cancer and exposure to metals: the epidemiological evidence. Methods Mol Biol 472:139–167

Yan S, Ling Q, Bao Z (2007) Metals contamination in soils and vegetables in metal smelter contaminated sites in Huangshi, China. Bull Environ Contam Toxicol 79(4):361–366

Yang F, Tan J, Zhao Q, Du Z, He K, Ma Y, Duan F, Chen G, Zhao Q (2011) Characteristics of $PM_{2.5}$ speciation in representative megacities and across China. Atmos Chem Phys 11(11):5207–5219

Yang G, Wang Y, Zeng Y, Gao GF, Liang X, Zhou M, Wan X, Yu S, Jiang Y, Naghavi M, Vos T, Wang H, Lopez AD, Murray CJL (2013) Rapid health transition in China, 1990–2010: findings from the Global Burden of Disease Study 2010. Lancet 381(9882):1987–2015

Yatkin S, Bayram A (2008) Source apportionment of PM_{10} and $PM_{2.5}$ using positive matrix factorization and chemical mass balance in Izmir, Turkey. Sci Total Environ 390(1):109–123

Yih SW, Wang CT (1979) Tungsten: sources, metallurgy, properties, and applications. Plenum Publishing Corporation, New York

You S, Yao Z, Dai Y, Wang CH (2017) A comparison of PM exposure related to emission hotspots in a hot and humid urban environment: concentrations, compositions, respiratory deposition, and potential health risks. Sci Total Environ 59–60:464–473

Yu J, Yao S, Chen R, Zhu K, Yu L (2005) A quantitative integrated evaluation of sustainable development of mineral resources of a mining city: a case study of Huangshi, Eastern China. Resour Policy 30(1):7–19

Zhang YL, Cao F (2015) Fine particulate matter ($PM_{2.5}$) in China at a city level. Sci Rep UK 5:14884. https://doi.org/10.1038/srep14884

Zheng M, Salmon LG, Schauer JJ, Zeng L, Kiang C, Zhang Y, Cass GR (2005) Seasonal trends in $PM_{2.5}$ source contributions in Beijing, China. Atmos Environ 39(22):3967–3976