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RESEARCH ARTICLE

Acid-extractable heavy metals in $PM_{2.5}$ over Xi'an, China: seasonal distribution and meteorological influence

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Abstract

To investigate the acid-extractable heavy metals in fine particulate matter ($PM_{2.5}$) over Xi'an, China, 24-h $PM_{2.5}$ samples were collected every 3 days from December 2015 through November 2016. The bioavailable fraction, termed here the bioavailability index (BI), of $PM_{2.5}$-bound metal (As, Ba, Cd, Co, Cu, Mn, Ni, Pb, Ti, V, and Zn) and potential influencing factors, including relative humidity, temperature, air pressure, wind speed, visibility, $PM_{2.5}$, and SO_2 concentrations, were assessed in this study. The annual average $PM_{2.5}$ concentration was 50.6 ± 35.6 μg m^{-3}, 1.5 times higher than the Chinese national secondary standard. Zn, Ti, and As were the most abundant elements of those analyzed in the $PM_{2.5}$ samples, accounting for 72.1% of total quantity. The seasonal variations and enrichment factor analysis of heavy metals revealed that coal combustion in winter was a crucial source of Pb, Co, Cu, and Zn; and dust resuspension in spring contributed considerable Mn, Ti, and V. The acid-extractable fractions of the measured metals varied. Pb, Cu, Mn, and Zn exhibited relatively high acid-extractable concentrations and BI values. Pb was mostly in the acid-extractable fraction in $PM_{2.5}$, with a mean BI value of 66.7%, the highest in summer (69.8%) and lowest in winter (63.7%). Moreover, the BIs of $PM_{2.5}$-bound heavy metals were inversely related to temperature and wind speed, whereas positively correlated with relative humidity, SO_2, and $PM_{2.5}$ concentration in this study. This study assessed the seasonal distribution and meteorological influence of acid-extractable heavy metals, providing a deeper understanding of atmospheric heavy metal pollution in Xi'an, China.

Keywords $PM_{2.5}$ · Heavy metals · Acid-extractable fractions · Bioavailability index · Meteorological factors

Highlights
- Zn, Ti, and As were the most abundant heavy metals in $PM_{2.5}$ in Xi'an.
- Characteristic and influence factor of acid-extractable heavy metals were evaluated.
- Acid-extractable heavy metals showed the highest levels in winter or spring.
- Pb exhibited the highest acid-extractable level and bioavailable fraction.
- Bioavailable fractions correlated to T and WS negatively, to RH and SO_2 positively.

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Introduction

Many cities in China have experienced episodes of high levels of $PM_{2.5}$, which has become a topic of increasing social concern (Gao et al. 2014; Xu et al. 2016). $PM_{2.5}$ causes great harm to the health of living beings and is closely associated with haze (Cao et al. 2011; Shen et al. 2016b). The complex chemicals comprising $PM_{2.5}$ have large specific surface areas and include organic substances, sulfate, nitrate, ammonium, organic carbon (OC), and elemental carbon (EC), and inhaling these chemicals into the human body is extremely hazardous (Feng et al. 2016; Li et al. 2016b; Xu et al. 2017a). Generally, heavy metals are toxic to the environment and human health (Liu et al. 2017). As particle size of particle matter (PM) decreases, the proportion of heavy metals in PM increases, and the negative effects on environmental quality and human health increase considerably (Liu et al. 2018a; Pongpiachan and Iijima 2016; Tan et al. 2016).

Accumulating evidences from toxicological and epidemiological studies (Li et al. 2016a, 2017) suggest that

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heavy metals are the main toxic components in $PM_{2.5}$; this is particularly true of their acid-extractable fractions, which are not biodegradable and may also be enriched in living organisms and thus further endanger human health through the food chain (Li et al. 2015; Liu et al. 2018b). To our knowledge, the toxicity, migration, and circulation processes of various heavy metal forms in the ecosystem differ (Betha et al. 2014; Kara et al. 2014), and these differences can provide crucial information to gain a comprehensive understanding of the pollution characteristics and health effects of airborne metals. Toxicological experiments have also revealed that heavy metal dissolution and absorption in the organisms depend largely on the bioavailability of such metals, which is determined mainly by their solubility (particularly in water) (Amodio et al. 2014; Yang et al. 2017), surface properties of $PM_{2.5}$, and strength of chemical bonds with other elements (Schleicher et al. 2011).

The European Community Bureau of Reference (BCR) sequential extraction method was proposed by Commission of the European Communities in 1987 on the basis of numerous experiments (Ure et al. 1993). The method divides an elemental form into reducible fraction, oxidizable fraction, residual fraction, and weak acid-soluble fraction (also called the acid-extractable fraction). Among the four chemical fractions of heavy metals, the acid-extractable fraction is mainly adsorbed on the surface of particles through relatively weak electrostatic interaction (Li et al. 2017; Sah et al. 2019). This fraction shows high bioavailability for environmental receptors and is more absorbed by food and objects, and deposited on their surfaces through ion exchange; when ingested, the fraction is exposed to the human body and leads to malignant diseases (Li et al. 2014; Sun et al. 2014). Therefore, evaluating the bioavailability of heavy metals in $PM_{2.5}$ is crucial and can be performed using multistep extraction to determine the ratio of the acid-extractable fraction to the total elemental amount (Huang et al. 2014; Tagliani et al. 2017). The higher this ratio is for a given metal, the easier the metal is absorbed by organisms and the greater are the damages incurred in $PM_{2.5}$. Most previous studies have focused on source analysis and the distributions of temporal and spatial characteristics of the total quantities of heavy metals (Gao and Ji 2018; Wang et al. 2018). Studies on the bioavailability of heavy metals and their harm to the environment and human health remain insufficient.

Xi'an, a major city in Northwestern China, is located in the center of the Guanzhong Plain, surrounded by the Loess Plateau and Qinling Mountains. Although trace metals in $PM_{2.5}$ are investigated to determine their sources and environmental and health effects (Cao et al. 2011; Liu et al. 2018a; Shen et al. 2016b; Sun et al. 2019; Xu et al. 2017b; Zhang et al. 2014), few studies have focused on acid-extractable metal levels. The main objectives of this study are to (1) investigate the seasonal variations of acid-extractable metals (As, Ba, Cd, Co, Cu, Mn, Ni, Pb, Ti, V, and Zn) in $PM_{2.5}$ and (2) determine the bioavailability index (BI) of heavy metals and characterize its relationship with meteorological factors. The results of this study can offer valuable information to policymakers for scientifically evaluating the air quality in Xi'an and formulating control and prevention measures for heavy metals in $PM_{2.5}$.

Materials and methods

Sample collection

Ambient $PM_{2.5}$ samples were collected from the Xingqing Campus of Xi'an Jiaotong University (108° 59′ 7.30″ E, 34° 14′ 37.75″ N) in Xi'an, China. The air quality in the study area is affected by emissions from high levels of traffic as well as industrial pollutants emitted from urban areas (Fig. 1).

The $PM_{2.5}$ samples were collected on quartz-fiber filters (20.3 cm × 20.4 cm) using a high-volume atmospheric $PM_{2.5}$ sampler (HVS-$PM_{2.5}$, Thermo Fisher Scientific, Waltham, MA, USA) at approximately 1.13 m^3 min^{-1}; 24-h $PM_{2.5}$ samples were collected every 3 days (from 10:00 a.m. to 10:00 a.m. the following day) from December 2015 through November 2016. The sampling head was placed approximately 20 m above the ground. All the filters used in this study were previously baked for 3 h at 800 °C (Shen et al. 2017). A total of 122 analytical samples and 12 field blank samples (collected once a month) were collected during the sampling period. All loaded samples were stored in a freezer at − 4 °C to prevent any evaporation of volatile compounds before chemical analysis. A detailed description of the filter weighing process before and after sampling was provided by Shen et al. (2009).

To study temporal variation characteristics, the months of December, January, and February were considered winter, and other seasons were defined as successive 3-month intervals. The meteorological data (temperature [*T*], relative humidity [RH], wind speed [WS], air pressure [AP], and visibility) in Xi'an during the sampling period were obtained from Xi'an Xianyang International Airport station on the Weather Underground (http://www.wunderground.com), which was collected based on the technical specifications of the civil aviation automatic meteorological observing systems (Civil Aviation Administration of China 2013; Air Traffic Management Office of the Civil Aviation Administration of China 2018). SO_2 concentrations were obtained from the national automatic air quality monitoring stations in Xi'an from China National Environmental Monitoring Centre (http://106.37.208.233:20035/).

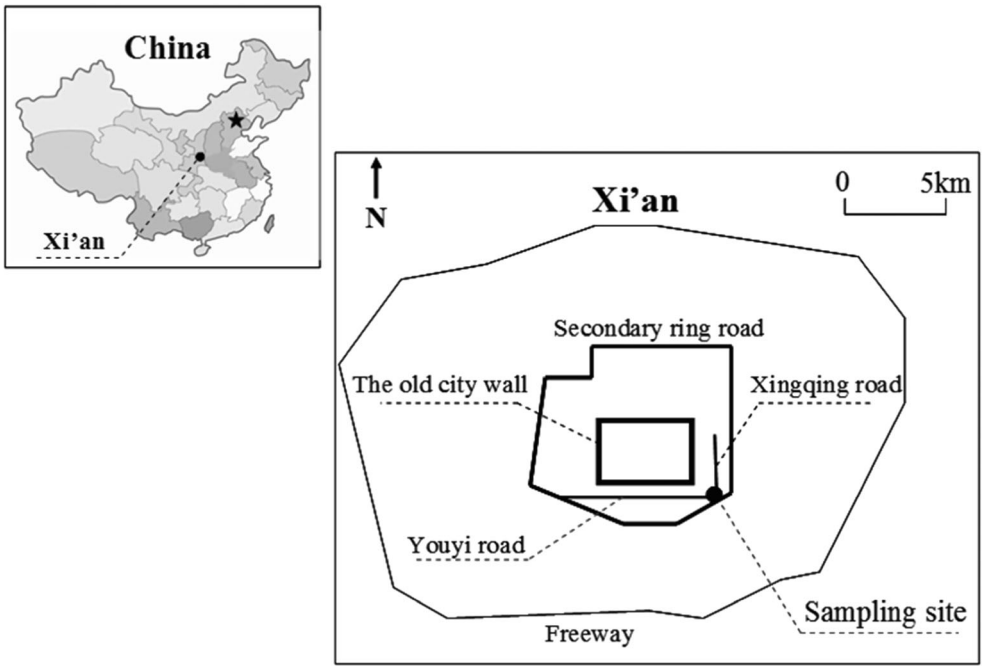

Fig. 1 Location of sampling site

Elemental analysis

A 47-mm-diameter punch was cut from the parent $PM_{2.5}$ sample for analysis of 11 heavy metals (i.e., As, Ba, Cd, Co, Cu, Mn, Ni, Pb, Ti, V, and Zn) and Fe, the reference element. One-fourth (1.04 cm^2) of the punch was cut into fragments and then placed into a Teflon vessel for acid digestion. Each sample was added to 6 mL of HNO_3:HCl (3:1 v/v) and 1 mL hydrofluoric acid. A microwave digestion unit (Multiwave Go, Anton Paar, Graz, Austria) with temperature control was used to digest the samples for measurement of total metals. The samples were placed into vials, which were screwed on the digestion unit and allowed to stand for 30 min before being placed into the microwave digestion unit. The samples were digested using the following two-stage digestion program: In stage 1, the digestion temperatures gradually increased from 120 to 160 °C, 180 °C, and 200 °C over 45 min. In stage 2, the sample digestion solution was evaporated on a hot plate (120 °C) until the volume was reduced to 1 mL. The digested solution was then diluted to 10 mL with deionized water (resistivity = 18.3 MΩ cm).

Extraction was performed using BCR sequential extraction method. This procedure has been used in several studies (Li et al. 2013b, 2014, 2015) to extract the acid-extractable fractions of heavy metals. In brief, one-fourth of a 47-mm-diameter punch was added to 10 mL of acetic acid (0.11 M) in 50-mL polyethylene centrifuge tubes and subsequently shaken at 180 rpm and a temperature of 20 °C for 16 h. The extracts were then separated from the residue through centrifugation for 10 min at 6000 rpm and diluted to 10 mL with deionized water (resistivity = 18.3 MΩ cm).

The total heavy metal and acid-extractable fraction solutions were both filtered for debris (Nylon 66, 0.22 μm, Jinteng, Tianjin, China) and then analyzed for elemental concentrations with an inductively coupled plasma–atomic emission spectrometer (Shimadzu, Kyoto, Japan). Blank tests using standard solution were performed before the target sample analysis.

Enrichment factors

The enrichment factor (EF) is a characteristic value indicating the degree of enrichment of elements in PM and is used to determine whether an element is derived from a natural source. Many studies have used the EF to analyze the sources of elements in anthropogenic systems (Kong et al. 2014; Liu et al. 2018a). According to the following Eq. (1), EF values in this study were calculated relative to the reference crustal element, Fe, which is less affected by anthropogenic pollution (Li et al. 2016a; Niu et al. 2015):

$$\mathrm{EF} = \frac{(C_n/C_{\mathrm{ref}})_{\mathrm{sample}}}{(C_n/C_{\mathrm{ref}})_{\mathrm{background}}} \quad (1)$$

where C_n and C_{ref} are the concentrations of element n and the reference element (Fe), respectively, in a $PM_{2.5}$ sample and the background soil. The background content in the formula is adopted from the Chinese background soil value. EFs of < 1, 1–10, and > 10 indicate that the target element is derived from crustal weathering and no enrichment occurred in the environment, that the relative enrichment of the element is affected by human activity, and that the element in the sample is primarily

anthropogenic, respectively (Cao et al. 2011; Reimann and De Caritat 2000; Wang et al. 2018).

Bioavailability index

For the assessment of heavy metals hazardous to human health, the acid-extractable fraction ($C_{\text{acid-extractable fraction}}$) relative to the total metal concentration ($C_{\text{total amount}}$) was used as a bioavailability index (BI) of heavy metals (Yadav and Satsangi 2013) according to the following Eq. (2):

$$\mathrm{BI} = \frac{C_{\text{acid-extractable fraction}}}{C_{\text{total amount}}} \times 100\% \quad (2)$$

Bioavailability is classified into three categories based on BI values. BI values of < 30%, 30–50%, and > 50% represent low, medium, and high, respectively.

Statistical analysis

A Pearson's correlation coefficient matrix was constructed through correlation analysis performed in SPSS (version 23.0).

Quality assurance and quality control

The filters were folded and packed with aluminum foil after sampling and subsequently placed in a freezer at − 4 °C. Each filter was weighed three times before and after sampling, and the average value (minus the blank values) was reported. The nitric acid used in this study was of chromatographic grade, and the other reagents were of analytical grade. Each batch was analyzed with at least two blank samples to determine the accuracy of the method; a standard curve was established, and the correlation coefficient (r) of the standard sample was > 0.999. Heavy metal solutions were prepared with ultrapure water (resistivity = 18.3 MΩ cm). The recoveries of the measured elements ranged from 83 to 114%.

Results and discussion

$PM_{2.5}$ and heavy metal concentrations

The monthly $PM_{2.5}$ concentrations and meteorological conditions (RH, visibility, and WS) during the sampling period are summarized in Fig. 2. The $PM_{2.5}$ mass concentration varied greatly from 7.35 to 233 μg m^{-3}, with an average value of 50.6 ± 35.6 μg m^{-3}, approximately 1.5 times the guideline for annual $PM_{2.5}$ (35 μg m^{-3}) set by the Chinese National Ambient Air Quality Standards (NAAQS) (GB3095-2012). For 56.2% of the sampling days, the daily average $PM_{2.5}$ concentration exceeded the 24-h standard (75 μg m^{-3}) of the NAAQS. The average $PM_{2.5}$ concentrations in winter and spring were 77.1 ± 23.5 μg m^{-3} and 62.1 ± 44.4 μg m^{-3}, respectively, and significantly higher than those in summer (23.6 ± 5.3 μg m^{-3}) and fall (24.3 ± 8.6 μg m^{-3}). During the heating period (from November 15 to March 15), $PM_{2.5}$ concentration always exceeded the national daily standard (75 μg m^{-3}), resulting in severe haze in Xi'an. This can be attributed to the adverse meteorological conditions (high pressure and severe inversion), which induce atmospheric stability, and the enhancement of $PM_{2.5}$ emissions (burning of coal and biomass). Such temporal differences are consistent with the results of Gao and Ji (2018) from Beijing and Wang et al. (2015) from Xi'an, China. The average WS and visibility recorded differed significantly in winter and summer. As expected, low WS and visibility were observed in winter, and the lowest WS, i.e., 1.5 m s^{-1} (half the WS value in July) was recorded in November, resulting in the air pollution accumulation.

The total elemental concentrations in $PM_{2.5}$ in Xi'an measured during this study are listed in Table 1. The mass concentrations of Zn and Ti in $PM_{2.5}$ both accounted for 27.9% of the total concentration of all tested heavy metals, followed by As (16.2%). The total concentrations of these three heavy metals accounted for 72.1% of the total content. The annual average concentration of Pb was 34.1 ng m^{-3}, far below the NAAQS guideline (500 ng m^{-3}). Other particulate-bound element concentrations are compared with the NAAQS and the World Health Organization (WHO) guidelines as follows (WHO 2005): The annual average As concentration was 116 ng m^{-3}, considerably higher than the NAAQS (6 ng m^{-3}) and WHO (6 ng m^{-3}) guidelines. Cd concentrations in all the samples exceeded 3.3 times the NAAQS guideline (5 ng m^{-3}). Together, these two findings suggested that As and Cd pollutions were severe in this area, which was consistent with the actual state of such pollution in Xi'an (Chifflet et al. 2018; Dai et al. 2019). Coal combustion (coal-fired power plants, factory boilers, and winter heating supply) around and in Xi'an was the important source for these two elements (Chifflet et al. 2018; Schleicher et al. 2011; Tan et al. 2016). Besides, motor vehicle exhaust is also an important source of urban trace metal pollution in $PM_{2.5}$, which mainly involves direct emissions of Cd bound to exhaust particles, lubricating oil additives, and the wear of other vehicle parts (Hu et al. 2012).

Seasonal variations and EFs of heavy metals

Most of the 11 measured heavy metals exhibited the highest concentration in winter or spring (except for Ni). Mn, V, and Ti concentrations exhibited the same seasonal pattern-higher levels in spring than in other seasons-mainly because of dust resuspension (Hao et al. 2018; Schleicher et al. 2011) resulting from the predominance of crustal earth sources in spring,

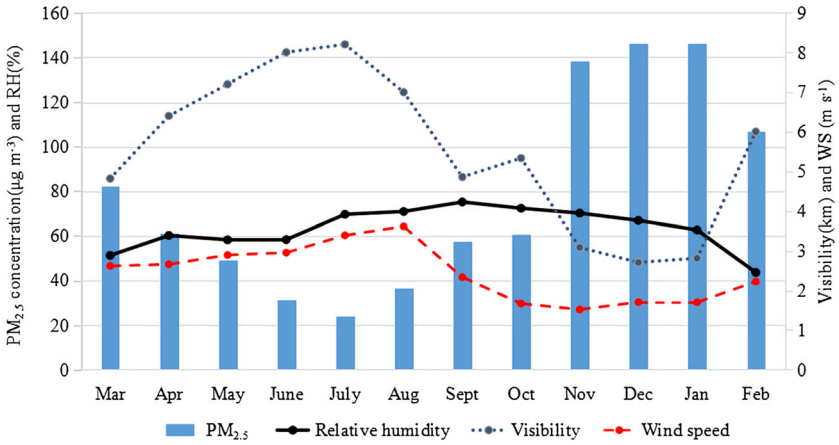

Fig. 2 $PM_{2.5}$ concentrations and meteorological data during the sampling period (RH relative humidity, WS wind speed)

particularly on dust storm days. During the heating period, the significant enhanced concentrations of Pb, Co, Cu, and Zn occurred (Poulakis et al. 2015). The levels of Pb in $PM_{2.5}$ in winter increased 2.8 times that in summer because of the prolific combustion of coal for heating (Xu et al. 2012). Coal-fired emissions may contribute to Co, Cu, and Zn in $PM_{2.5}$ to some extent.

The EFs of $PM_{2.5}$-associated heavy metals during the sampling period in Xi'an are shown in Fig. 3. The EFs of Cd and As in $PM_{2.5}$ were greater than 100, indicating that these elements were predominantly derived from human activities, such as steel smelting, coal combustion, and vehicle emissions (Chifflet et al. 2018). These metals were easily concentrated in $PM_{2.5}$ and thus could be transported over long distances (Amodio et al. 2014; Tian et al. 2016). Cd displayed the highest EF value among all the studied metals (average = 4566), implying that it was strongly linked with metal smelting and other anthropogenic sources. The EFs of Zn, Cu, and Pb were less than 100 but greater than 10, and the EFs of Co and Ni were close to 10, indicating that these heavy metals were moderately enriched and affected by human activities (Cao et al. 2011). The EFs of Ba, V, Mn, and Ti were all slightly higher than 1, suggesting natural emission to be the primary source of these elements, which was consistent with the conclusions mentioned above (Kara et al. 2014). It is noticeable that V affected by the human activities was slight in this study. V is usually served as a typical tracer of heavy oil combustion, especially derived from ship emissions in coastal areas (Poulakis et al. 2015; Tan et al. 2016; Wang et al. 2018). Xi'an is located the inland of northwest China, far from the ship emissions. Besides, a vehicle restriction policy was issued in 2014 to limit heavy diesel vehicle emissions (Qiu et al. 2016; Zhang et al. 2014). Therefore, V concentration and its enrichment factor were quite low in the studied area.

Characteristics of acid-extractable heavy metals in $PM_{2.5}$

Acid-extractable heavy metals adsorbing to particle surfaces can be easily released into aqueous solutions. Acid-extractable forms are highly bioavailable and pose the greatest risks to the human body (Mukhtar and Limbeck 2013; Ventura et al.

Table 1 Concentrations (average ± standard deviation) of heavy metals in $PM_{2.5}$

Metal	Total elemental concentration (ng m^{-3})					Acid-extractable fraction concentration (ng m^{-3})				
	Spring	Summer	Fall	Winter	Average	Spring	Summer	Fall	Winter	Average
As	142 ± 13.7	90.9 ± 4.32	89.8 ± 5.43	121 ± 15.7	116 ± 35.9	12.8 ± 4.32	5.07 ± 1.56	7.05 ± 1.40	13.4 ± 0.34	9.00 ± 6.33
Ba	54.3 ± 15.2	53.5 ± 18.3	43.2 ± 3.94	44.5 ± 17.4	47.1 ± 30.6	8.88 ± 4.21	5.24 ± 3.12	5.01 ± 0.31	7.39 ± 4.75	7.35 ± 6.68
Cd	19.3 ± 5.45	12.3 ± 2.76	11.1 ± 3.12	20.3 ± 4.34	16.5 ± 5.83	0.92 ± 0.44	0.58 ± 0.11	0.79 ± 0.21	1.87 ± 0.62	1.11 ± 0.70
Co	4.50 ± 2.22	3.01 ± 1.54	2.38 ± 1.07	6.07 ± 2.79	4.42 ± 2.85	0.36 ± 0.19	0.14 ± 0.10	0.22 ± 0.10	0.77 ± 0.41	0.42 ± 0.32
Cu	35.9 ± 8.04	35.0 ± 7.46	27.7 ± 10.9	49.8 ± 24.7	41.3 ± 37.4	18.0 ± 4.27	16.7 ± 2.35	16.5 ± 0.47	17.7 ± 5.57	17.6 ± 2.49
Mn	41.2 ± 13.1	22.6 ± 4.73	20.2 ± 4.77	33.7 ± 9.04	30.2 ± 12.1	14.6 ± 4.39	7.12 ± 2.28	10.6 ± 3.22	12.0 ± 4.12	11.4 ± 6.58
Ni	12.6 ± 2.78	12.7 ± 3.16	10.4 ± 0.91	10.5 ± 4.27	10.6 ± 5.74	1.95 ± 0.37	1.84 ± 0.13	1.87 ± 0.33	1.71 ± 0.46	1.67 ± 0.83
Pb	32.1 ± 14.7	18.6 ± 6.46	24.1 ± 7.34	52.4 ± 23.2	34.1 ± 20.6	20.9 ± 7.68	14.1 ± 7.67	16.9 ± 6.00	32.0 ± 12.6	22.1 ± 11.6
Ti	243 ± 57.6	163 ± 47.5	151 ± 20.9	220 ± 44.3	200 ± 59.3	5.94 ± 3.71	3.99 ± 1.01	3.75 ± 0.55	4.72 ± 1.72	4.71 ± 2.39
V	8.58 ± 4.27	4.85 ± 0.74	3.96 ± 0.57	5.80 ± 1.22	6.00 ± 2.95	1.14 ± 0.35	0.91 ± 0.09	0.97 ± 0.16	1.06 ± 0.33	1.03 ± 0.45
Zn	160 ± 52.5	137 ± 55.2	192 ± 6.92	211 ± 64.1	200 ± 61.2	75.6 ± 55.4	50.7 ± 36.2	83.3 ± 25.3	90.4 ± 40.7	77.4 ± 25.0

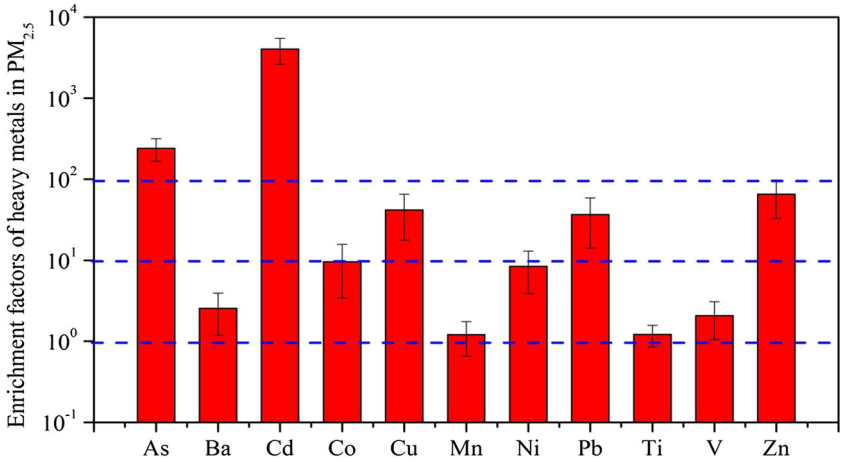

Fig. 3 Enrichment factors of heavy metals in $PM_{2.5}$

2017). The concentrations of these acid-extractable heavy metals are also presented in Table 1. The acid-extractable fractions of Cd, Co, Pb, and Zn demonstrated typical seasonal variation, with higher concentrations in winter. The concentrations of acid-extractable As and Ba in winter and spring were higher than those in autumn and summer. By contrast, acid-extractable Mn, Ti, and V exhibited significantly higher concentrations in spring, whereas the acid-extractable fraction concentrations of Cu and Ni remained relatively stable throughout the four seasons (Sah et al. 2019). Among the analyzed elements, As, Pb, Cu, and Zn are discussed in detail in this section because of their relatively high concentrations and harmfulness to human health (Liu et al. 2018a).

The annual average concentration of the acid-extractable fraction of As in $PM_{2.5}$ in Xi'an was 9.0 ng m^{-3}, comparable to a result from urban $PM_{2.5}$ in Beijing (13 ng m^{-3}) (Schleicher et al. 2011). Considering only the acid-extractable fraction of As concentration, 63.1% of samples still exceeded the NAAQS (6 ng m^{-3}) and WHO (6 ng m^{-3}) guidelines. Therefore, As was considered an important element for assessing the toxicity of $PM_{2.5}$ in this area. The lowest acid-extractable As concentrations were observed in summer, with an average value of 5.1 ng m^{-3}, whereas winter concentrations were the highest (average 13.4 ng m^{-3}); this trend is consistent with that of the total concentration of As. The acid-extractable fraction of Pb was significantly higher in winter (32.0 ng m^{-3}) than spring (20.9 ng m^{-3}), followed by the fractions in autumn (16.9 ng m^{-3}) and summer (14.1 ng m^{-3}); this result confirmed coal combustion as the main source of Pb. Gong et al. (2010) investigated coal ash dumps in China and proved coal combustion to be a source of heavy metals in PM, particularly As and Pb. Moreover, the stagnant wind conditions and scarcity of rain in winter led to the relatively high accumulation of acid-extractable elements in $PM_{2.5}$ (Voutsa et al. 2015). The acid-extractable concentrations of Cu were indicative of a stable pattern throughout the entire year. Cu is suspected to be related to vehicle emission, smelting furnaces, and high-temperature smelting operations and thus exhibit minimal seasonal difference in its acid-extractable levels (Amodio et al. 2014; Li et al. 2015). The acid-extractable fraction of Zn varied greatly by season, with a mean concentration of 77.4 ng m^{-3}, exhibiting the following seasonal pattern: winter (90.4 ng m^{-3}) > fall (83.8 ng m^{-3}) > spring (75.6 ng m^{-3}) > summer (50.7 ng m^{-3}). This pattern is consistent with the seasonal variation of total Zn. Zn in $PM_{2.5}$ typically originates from the metal smelting industry and vehicle tire wear (Zhang et al. 2014). The elevated acid-extractable Zn concentrations observed in winter might be related to the more frequent occurrence of unfavorable dispersion conditions (Hao et al. 2018). And it was also affected by other multiple factors, such as the acidity and alkalinity of PM, secondary conversion process of primary air pollution sources, and acidification process of air (Hsu et al. 2010).

BI of heavy metals

The acid-extractable fractions of the total elemental amounts, expressed as BI, are presented in Fig. 4. The highest BI was noted for Pb, with an annual average value of 66.7%, indicating that Pb existed mainly in the weak acid-binding state. Because Pb showed the highest BI, it might be the most available element for physiological activity and thus enter the digestive system and be absorbed by the human stomach most easily (Hu et al. 2012). Pb in PM is mainly in the forms of sulfates, carbonates, oxides, nitrates, halides, and organic lead compounds; among these, nitrates are readily soluble in water (Duan and Tan 2013). Although leaded gasoline was banned in Xi'an in 2000 (Schleicher et al. 2011), Pb from fossil fuel combustion emissions persisted in $PM_{2.5}$. The particles from vehicular exhaust emissions are easily acidified in the atmosphere to form unstable nitrates and other soluble compounds (Heal et al. 2005; Shen et al. 2016a). Pb discharged from traffic sources can rapidly solidify with $(NH_4)_2SO_4$ aerosol to form soluble sulfate particles (Li et al. 2013a). On the basis of the energy consumption in Xi'an, coal can be considered the most important source of energy in winter, and coal

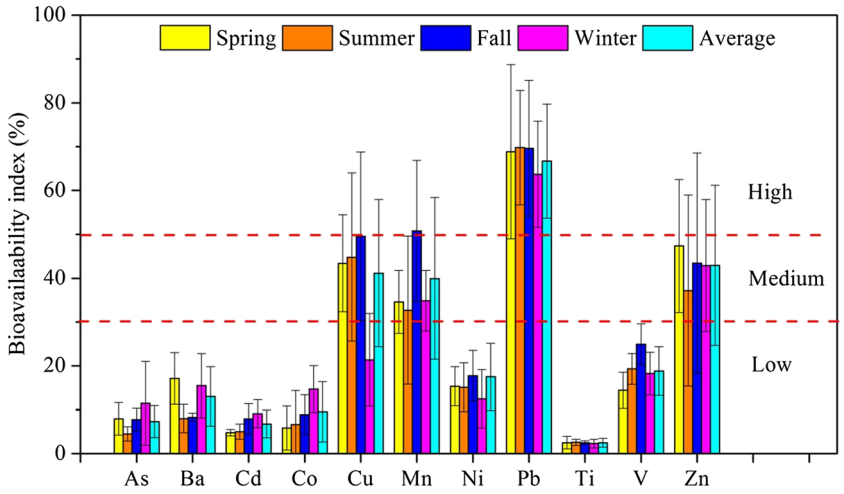

Fig. 4 Seasonal variation in the bioavailability indices of heavy metals in $PM_{2.5}$

combustion emission is the main source of Pb in $PM_{2.5}$ (Duan and Tan 2013). As the contribution of coal combustion increased in winter, the contribution of motor vehicle to Pb in $PM_{2.5}$ decreased. Therefore, the BIs of Pb in $PM_{2.5}$ displayed the highest level in summer (69.8%) and the lowest in winter (63.7%).

Zn, Cu, and Mn exhibited the higher proportions of the acid-extractable fractions, accounting for 42.9%, 41.2%, and 40.0%, respectively, of their individual total amounts and medium bioavailability. Zn contributed 50.3% of the acid-extractable concentration of all elements, indicating that it may pose a higher risk to human health than any other elements. Meanwhile, V, Ni, and Ba exhibited the low bioavailability levels, with mean acid-extractable fraction percentages of 18.8%, 17.5%, and 13.0%, respectively. Co, As, Cd, and Ti showed the lowest bioavailability values, with mean BI values of 9.5%, 7.3%, 6.8%, and 2.5%, respectively. Although the crustal element Ti contributed 28.3% to the total concentrations of the studied elements, the lower concentration of its acid-extractable fraction (4.71 ng m^{-3}) and BI (2.5%) was found than other elements, meaning that Ti posed less of a health concern in the studies area.

Factors influencing BI

The acid-extractable fractions of heavy metals are dependent upon meteorological factors and the concentrations of certain pollutant gases (Li et al. 2017). The RH (relative humidity), SO_2 concentration, $PM_{2.5}$ concentration, T (temperature), AP (air pressure), WS (wind speed), and visibility exerted dissimilar influences on the BIs of heavy metals in $PM_{2.5}$ in this study. The correlations (r value) are presented in Table 2.

Significant positive correlations were found between average RH and BI levels of all metals except Ba. Clear associations were noted with Cd, Co, Mn, Ni, and V (r = 0.246–0.524). High RH may increase the BI of heavy metals in the atmosphere because it likely causes particles to contain more water-soluble metal species (Chen et al. 2016; Luo et al. 2019). Gao and Ji (2018) demonstrated that the formation of secondary aerosol species and secondary organic compounds could be enhanced under high RH. Soluble heavy metals in the atmosphere easily react with nitrate and sulfate in $PM_{2.5}$ to form water-soluble metal sulfates and nitrates (Ming et al. 2017; Niu et al. 2015). Thus, water vapor in the air promoted the formation of sulfates and nitrates and increased the acid-extractable metal fractions (Li et al. 2010, 2019).

Correlation analysis revealed that BIs were positively correlated with atmospheric SO_2 concentrations for most elements. As, Ba, Cd, and Co exhibited strong positive correlations. Cheng et al. (2016) demonstrated that SO_2 could be adsorbed onto and enriched within atmospheric PM; chemical reactions occurring in PM could catalytically oxidize to form sulfates. In addition, Li et al. (2013b) indicated that atmospheric sulfates are derived mostly from wet deposition; moreover, acidic SO_4^{2-} aerosol is more conducive to the conversion of metals from oxidizable fractions and reducible fractions to acid-extractable fractions (Zhang et al. 2013, 2015). On analyzing summer data, the positive correlations between BIs and SO_2 concentrations were relatively strong (for all tested elements, r = 0.072–0.398), because of the higher RH and more intense solar radiation in summer, increasing the production of secondary sulfates through reactions between heavy metals and acidic ions in atmospheric reaction processes (Benetello et al. 2018; Li et al. 2017, 2019; Schleicher et al. 2011). This conclusion confirmed the results of the previously mentioned RH and BI correlation analysis.

$PM_{2.5}$ concentration exhibited mainly positive correlations with BI for several of the measured heavy metals. The strongest positive relationships were found for As, Cd, and Co. During coal combustion, heavy metals are

Table 2 Pearson's correlation coefficients (r) between BIs of metals and influencing factors

	RH	SO_2	$PM_{2.5}$	T	AP	WS	Visibility
As	0.016	0.443**	0.318**	− 0.307**	0.285**	− 0.187*	− 0.216*
Ba	− 0.540**	0.181*	0.034	0.170	0.136	− 0.067	0.091
Cd	0.406**	0.497**	0.427**	− 0.468**	0.454**	− 0.213*	− 0.377**
Co	0.246*	0.504**	0.387**	− 0.496**	0.386**	− 0.203*	− 0.266**
Cu	− 0.068	− 0.616**	− 0.468**	0.488**	− 0.381**	0.140	0.272**
Mn	0.236*	0.044	0.075	0.024	0.081	− 0.032	− 0.135
Ni	0.315**	− 0.246**	− 0.017	0.119	− 0.006	− 0.113	0.006
Pb	0.014	− 0.256*	− 0.280**	0.166	− 0.001	0.101	0.146
Ti	0.120	− 0.056	0.028	0.185*	− 0.180*	− 0.062	0.072
V	0.524**	0.082	0.118	0.014	0.114	0.007	− 0.182*
Zn	− 0.134	0.143	− 0.002	− 0.093	0.103	0.023	− 0.033

**Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

(*RH* relative humidity, *T* temperature, *AP* air pressure, *WS* wind speed)

easily enriched on the surface of particles, with numerous oxides, sulfides, and other inorganic forms in the atmosphere (Tian et al. 2015). Coal combustion also results in the emission of a high concentration of $PM_{2.5}$, its bounded As, Cd, and sulfates (Heal et al. 2005; Schleicher et al. 2011). This is supported by the stronger correlations between BIs of As and Cd and SO_2 concentrations in winter ($r = 0.270$ for As and 0.515 for Cd). Besides, correlation analysis revealed significant negative correlations between As, Cd, and Co BIs and T. T was not directly involved in elemental morphological transformation, but low T indirectly affected BI by leading to the consumption of coal for residential heating. The positive correlations of AP with the BI values of As, Cd, and Co can be attributed to the frequent occurrence of high pressure in winter.

WS mainly negatively correlated with the BIs of metals, particularly As, Cd, and Co, suggesting that the weak transportation and diffusion of air pollutants were important factors contributing to haze and led to the increase in BIs for those heavy metals (Benetello et al. 2018; Zhang et al. 2015). A similar conclusion could also be drawn regarding the correlations between visibility and BI. During haze episodes, secondary-organic-rich and inorganic-rich aerosols accumulate to high concentrations (Huang et al. 2014), and enhanced near-surface wind is conducive to the dispersion of air pollutants (Li et al. 2019; Prete et al. 2018). The analysis results revealed that the influences of meteorological parameters and gaseous air pollutants are exerted through highly complex and comprehensive processes. Therefore, the conclusion is that BI levels of heavy metals were mainly positively correlated with RH, SO_2, and $PM_{2.5}$ concentrations and negatively correlated with T, WS, and visibility in this study.

Conclusions

The characteristics and seasonal variations of the total amounts and acid-extractable fractions of $PM_{2.5}$-bound metals (As, Ba, Cd, Co, Cu, Mn, Ni, Pb, Ti, V, and Zn) were investigated in Xi'an, China in this study from 2015 to 2016. The annual average $PM_{2.5}$ concentration was 50.6 μg m^{-3}, 1.5 times higher than the annual guideline of Chinese NAAQS. Zn, Ti, and As were the most abundant elements among the studied metals in $PM_{2.5}$. Most elements showed significantly higher concentrations in winter or spring. Pb, Mn, Zn, and Cu exhibited relatively high acid-extractable fraction concentrations and strong bioavailability levels. The highest BI was observed for Pb, at approximately 66.7%, indicating the highest possibility to enter human food chains and corresponding health risks. Correlation analysis of BI influencing factors suggested that BIs were mostly negatively associated with T and WS. High RH, SO_2 concentration, and $PM_{2.5}$ concentration appeared to enhance the BIs of several heavy metals. This study suggests that future strategies for the control of $PM_{2.5}$-bound heavy metals should be based on city-specific industry and energy structure and consider not only the total levels of these heavy metals but also their chemical fractions and morphology.

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