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Seasonal Variation and Health Risk Assessment of Heavy Metals in $PM_{2.5}$ during Winter and Summer over Xi'an, China

Pingping Liu [1,2], Yali Lei [1], Huarui Ren [1], Jinjin Gao [1], Hongmei Xu [1], Zhenxing Shen [1,2,*], Qian Zhang [1], Chunli Zheng [1], Hongxia Liu [1], Renjian Zhang [3] and Hua Pan [1]

1 Department of Environmental Sciences and Engineering, Xi'an Jiaotong University, Xi'an 710049, China; liupingping@mail.xjtu.edu.cn (P.L.); 18682901770@163.com (Y.L.); renhuarui@stu.xjtu.edu.cn (H.R.); gaojinjin@stu.xjtu.edu.cn (J.G.); xuhongmei@xjtu.edu.cn (H.X.); zhangqian2011@stu.xjtu.edu.cn (Q.Z.); clzheng@mail.xjtu.edu.cn (C.Z.); hxliu72@mail.xjtu.edu.cn (H.L.); panhua@mail.xjtu.edu.cn (H.P.)

2 SKLLQG, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710061, China

3 Key Laboratory of Regional Climate-Environment for Temperate East Asia, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China; zrj@tea.ac.cn

* Correspondence: zxshen@mail.xjtu.edu.cn

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Abstract: In this study, 24 h $PM_{2.5}$ (particles with an equivalent diameter equal to or below 2.5 μm) samples were collected in winter and summer in Xi'an, Northwestern China to characterize the seasonal variations of eleven elements (As, Cd, Cr, Fe, K, Mn, Mo, Pb, Ni, Zn, and Cu) and to evaluate their health risks by using the US EPA (U.S. Environmental Protection Agency) method. Mass concentrations of the elements (except Ni) in winter were much higher than those in summer, with similar variations for both seasons. The levels of elements followed a decreasing order of K > Zn > Fe > Pb > Cr > As > Mn > Cu > Mo > Ni > Cd. According to the enrichment factor (EF) analysis, the highest EF value for Cd inferred that it should be linked with the metal smelting and other anthropogenic sources. In contrast, the EF values of K and Mn ($1 < EF < 5$) suggested that they were influenced by both natural and anthropogenic sources. The daily average exposure dose for children and adults by different exposure pathways were both ingestion > dermal contact > inhalation. The non-cancer risks for different exposure pathways showed different orders. The non-cancer risks (hazard quotients) were lower than the average risk threshold (1.0) except for As, Pb, and Cr, which require greater attention. Elements of As and Cr were higher than the cancer risk threshold value (1×10^{-6}), indicating that the cancer risks of $PM_{2.5}$ elements in Xi'an should be a concern.

Keywords: $PM_{2.5}$; metals; enrichment factor; non-cancer risk; cancer risk

PACS/MSC/JEL Classification: 42.68.Jg

1. Introduction

After reforming and opening up its markets, economy, urbanization, and energy consumption in China grew rapidly. Haze occurs frequently, and is one of the most important concerns in cities of China [1]. $PM_{2.5}$ (particles with an equivalent diameter equal to or below 2.5 μm) has been suggested to be closely associated with climatic change, agricultural production, natural ecosystem, and urban environment, especially haze, as well as adverse effects on human health [2,3]. China Ministry of Environmental Protection promulgated $PM_{2.5}$ standard in early 2012, but $PM_{2.5}$ concentrations in many cities are still not up to the standard. Health impact due to poor air quality and visual perception are

the main concerns of the general public nowadays. Therefore, the identification of dominant pollutant species in ambient air is crucial for making pollution control policies [4].

As the important chemical species in $PM_{2.5}$, elements could be an indicator for the change of $PM_{2.5}$ compositions and sources. Studies on the behavior of elements in PM could deepen the comprehension of toxicology characteristics, the mechanism of environmental influence of elements, as well as the emissions of different air pollution sources [5–7]. The main natural sources of elements in the atmosphere are soil dust, volcanic emissions, forest fire emissions, and meteoric dust. The anthropogenic sources are dominated by combustion of fuel oil and coal, metallurgical operations, and so on [8].

Many elements or metals are preferentially presented in finer particles [9], owing to lower densities, greater surface area per volume unit, and higher organic matter content in $PM_{2.5}$ [8,10]. Meanwhile, finer fractions of heavy metals could be more easily re-suspended and remain for longer times in the atmosphere [11] and more easily enter the human body through inhalation, ingestion, and dermal contact, resulting in adverse health effects [12]. A growing body of evidence has demonstrated that metals can accumulate in adipose tissue and the circulatory system of the body, and may affect the digestive, cardiovascular, and central nervous systems, and may also become a cofactor of other diseases [3,13]. For example, Pb exposure can lead to congenital malformations and lesions of the developing nervous system, causing important impairment in newborn's motor and cognitive abilities [14].

The study of health risk assessment of $PM_{2.5}$ in China started late, and the assessment of pollutant species and estimated area has been limited. At present, the main risk assessment of heavy metal pollutants are from Pb, Cu, Zn, Cd, Cr, As, Ni, and Hg, related to the assessment of regional polluted city surface soil (dust) and mining soil, diet, drinking water, groundwater, and atmospheric particles [15]. Previous research studies about elements in PM involved source identification, chemical composition, the relationship between elements in PM and the corresponding concentrations in blood and urine, as well as environmental exposure quantity and behavioral effects on different human groups [16]. Studies that consider health risk assessments of elements in $PM_{2.5}$ are very important in order to explore environmental health issue and strengthen environmental management [17]. The main purposes of this study are to determine $PM_{2.5}$ elemental concentrations and seasonal variations in Xi'an; identify natural and anthropogenic sources of elements in $PM_{2.5}$ by using enrichment factors; and assess $PM_{2.5}$ elemental cancer and non-cancer health risks.

2. Material and Methods

2.1. Description of Study Area

Xi'an, the largest city in Northwestern China, is located in the Guanzhong Plain at the southern edge of the Loess Plateau, which covers an area of 10,108 km^2 with a population of approximately 8.83 million, as of 2016. The sampling site (34.23° N, 108.98° E) is located in the southeastern area of Xi'an in a mixture of urban, vehicular, and residential areas (Figure 1). There is no obvious emission source around the sampling site.

2.2. Sample Collection

Twenty-four-hour (24 h) $PM_{2.5}$ samples (9:30 a.m. to 9:30 a.m. the next day, local time) were collected in two typical seasons (winter: 2 December 2008 to 24 February 2009 and summer: 6 June 2009 to 30 August 2009) on pre-combustion (780 °C, 3 h) quartz filters (20.3 cm × 25.4 cm) every six days. A high-volume $PM_{2.5}$ air sampler (HVS-$PM_{2.5}$, Thermo Fisher Scientific, Waltham, MA, USA) was operated on the flow rate of 1.1 m^3 min^{-1} in this study. The sampling head was placed about 20 m high above the ground. We collected 16 samples in winter and 15 samples in summer. Additionally, one summer field blank and one winter field blank were collected at the same site; the field blanks were used to account for any artifacts caused by gas absorption and background of filters. After sampling,

the exposed filters were placed in clean plastic cassettes and stored in a refrigerator at about 4 °C until analysis to minimize the evaporation of volatile components [18].

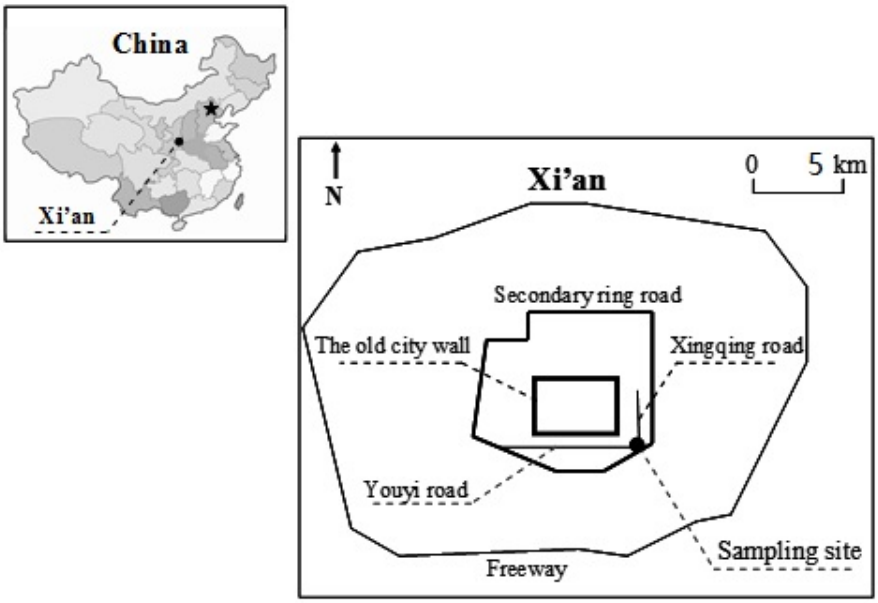

Figure 1. Location of sampling site.

2.3. Experimental Method

One-fourth of a 47-mm punch (an area of 4.337 cm^2) filter from $PM_{2.5}$ sample was placed in a Teflon digestion vessel for acid treatment. Each sample was treated with 8 mL of a mixture of HNO_3:HCl (1:3 v/v), 2 mL H_2O_2 (DC Chemical, EP grade), and 4 mL HF for 12 h to decompose the sample by microwave digestion. The digested solution was transferred into a Teflon cup, with 4 mL of perchloric acid added, then heated on the heating plate until it condensed into a droplet. Heating temperature was gradually increased to 120 °C, 160 °C, and 180 °C. After drying, the digested solution was diluted to 25 mL with 10% HNO_3 solution [19]. The solution was analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES, Shimadzu, Kyoto, Japan). The field blank filters were analyzed using these same procedures. The results of the blank analyses were corrected for the corresponding filter samples. Eleven elements: As, Cd, Cr, Fe, K, Mn, Mo, Pb, Ni, Zn, and Cu were determined in the present study. Accuracy tests according to standard materials (loess, GBW07408 and coal ash, GBW08401) were carried out in this study to guarantee the accuracy of the data. The recovery of this experiment ranged from 98% to 117% [20].

2.4. Source Identification

Potential sources of elements in $PM_{2.5}$ were evaluated by enrichment factor (EF), which is an important indicator of the disturbance to the natural environment caused by human activities to a certain extent [21]. By comparing measured values with soil background values, we can gain an understanding of the influence of human activity on the elements in aerosol [11]. The EF of each element was calculated relative to a reference crustal element Fe (it is a good indicator for crustal material due to being less affected from anthropogenic pollution) [22] by the following Equation (1):

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

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

If EF is 1 to 5, the element X can be considered to originate mainly from soil; if EF > 5, the element X mainly originated from human activities [23].

The mass concentration of certain element from anthropogenic source was calculated by Equation (2):

$$C_{non} = C - C_{Fe} \times (C/C_{Fe})_{crust} \quad (2)$$

where C_{non} is the mass concentration caused by anthropogenic sources of a certain element in $PM_{2.5}$. C is the mass concentration of a certain element in $PM_{2.5}$ during the sampling period. C_{Fe} is the mass concentration of Fe in $PM_{2.5}$ during the sampling period. $(C/C_{Fe})_{crust}$ is the ratio of mass concentration of a certain element and Fe in $PM_{2.5}$ in upper crustal matter [22].

2.5. Health Risk Assessment

This study adopted health risk assessment model from the US EPA (U.S. Environmental Protection Agency) to evaluate health risks of elements in $PM_{2.5}$. $PM_{2.5}$ causes health risks mainly in three ways: ingestion, inhalation, and dermal contact. The average daily dose (D, unit: mg kg^{-1} day^{-1}) through ingestion (D_{ing}), inhalation (D_{inh}), and dermal contact (D_{dermal}) can be calculated as follows [3,24]:

$$D_{ing} = C\left(mg{\cdot}kg^{-1}\right) \times \frac{IngR \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (3)$$

$$D_{inh} = C\left(mg{\cdot}kg^{-1}\right) \times \frac{InhR \times EF \times ED}{PEF \times BW \times AT} \quad (4)$$

$$D_{dermal} = C\left(mg{\cdot}kg^{-1}\right) \times \frac{SA \times SL \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (5)$$

where C is the concentration of the certain element in $PM_{2.5}$, mg kg^{-1}; IngR is the ingestion rate, 200 mg day^{-1} for children and 100 mg day^{-1} for adults [25]; InhR is the inhalation rate, 7.6 m^3 day^{-1} for children and 20 m^3 day^{-1} for adults [12,26,27]; EF is exposure frequency, 350 day $year^{-1}$ [12]; ED is exposure duration, 6 years for children and 30 years for adults [25]; SA is exposed skin area, 1800 cm^2 for children and 4350 cm^2 for adults [25,28,29]; SL is skin adherence factor, 0.2 mg cm^{-2} $event^{-1}$ for children and 0.07 mg cm^{-2} $event^{-1}$ for adults and event frequency is 1 event day^{-1} [25]; ABS is dermal absorption factor (unitless), 0.001 for all elements [25]; BW is average body weight, 15 kg for children and 60 kg for adults [24]; AT is averaging time, for non-carcinogens, AT = ED × 350 days; for carcinogens, AT = 70 × 350 = 24,500 days; PEF is the particle emission factor, which was calculated as:

$$PEF\left(m^3/kg\right) = \frac{Q}{C} \times \frac{3600s/h}{0.036 \times (1 - V) \times \left(\frac{U_m}{U_t}\right)^3 \times F(x)} \quad (6)$$

where Q/C is the inverse of the mean concentration at the center of the source square (g m^{-2} s per kg m^{-3}), which was selected as 90.80; V is the fraction of vegetable cover, which was selected as 0.5 (unitless) for soil dust and as 0.0 for road dust; U_m is the average annual windspeed (m s^{-1}), which was 2.00 m s^{-1} for Xi'an; U_t is the equivalent threshold value of windspeed at 10 m height, which was selected as 23.66 m s^{-1}; F(x) is the function dependent on U_m/U_t as 0.228 (unitless). This gave a value of 1.32×10^9 m^3 kg^{-1} for soil dust and 6.59×10^8 m^3 kg^{-1} for road dust in this study [3].

The non-cancer risk of eight elements (As, Cd, Cr, Mn, Pb, Ni, Zn, and Cu) through the above-mentioned three ways can be evaluated by hazard quotient (HQ) and Hazard Index (HI) [24]:

$$HQ = D/RfD \quad (7)$$

$$HI = \sum HQi \quad (8)$$

where RfD is the reference dose (mg kg^{-1} day^{-1}) of each element, which were obtained from the US EPA website [30]. HI can be calculated by adding the individual HQ_i (i means multiple-element or

multiple-route) to estimate the total non-cancer risks of all elements considered in the study. If the HI is lower than 1, then non-cancer effects are impossible. If the HI is equal to or higher than 1, adverse non-cancer health effects might be likely to appear. If the HI is greater than 10, a high chronic adverse risk exists [31].

The lifetime average daily dose (LADD) for the cancer risk (unit: mg kg^{-1} day^{-1}) of four elements (As, Cd, Cr, and Ni) in this study via inhalation was calculated by Equation (9) [3,32]:

$$LADD = \frac{C \times EF}{PEF \times AT} \times \left(\frac{InhR_{child} \times ED_{child}}{BW_{child}} + \frac{InhR_{adult} \times ED_{adult}}{BW_{adult}}\right) \quad (9)$$

The increased lifetime cancer risks (ILCR) are estimated by Equation (10) [33]:

$$ILCR = LADD \times SF \quad (10)$$

where SF is the cancer slope factor of a certain element, kg day mg^{-1}, which is obtained from the US EPA website [30]. The value of 10^{-6} is an internationally accepted precautionary or threshold value, above which the risk is unacceptable [25].

C (exposure-point concentration, mg kg^{-1}) in the Equations (3)–(5) and (9) refers to the upper limit of the 95% confidence interval (95% UCL) for the mean, which is also considered as the estimate of the "reasonable maximum exposure". In this study, $C_{95\%UCL}$ was calculated from the SPSS software (Model 19.0, IBM-SPSS, Armonk, NY, USA).

3. Results and Discussion

3.1. Characteristics of Elements in $PM_{2.5}$

The concentrations of the eleven elements (As, Cd, Cr, Fe, K, Mn, Mo, Pb, Ni, Zn, and Cu) bound to $PM_{2.5}$ are presented in Table 1. During the entire sampling period, with a large amount of straw used as the heating and cooking fuel in rural areas around Xi'an [34], the indicator of biomass combustion element, K, was the highest concentration of $PM_{2.5}$-bound element (357 ng m^{-3}), contributing to 43.5% of the elemental composition. The element found in the lowest concentration was Cd (8 ng m^{-3}), accounting for 0.09%. The annual average concentrations of other elements showed in the descending order: Zn > Fe > Pb > Cr > As > Mn > Cu > Mo > Ni. We can see that traffic and industrial elemental tracer-Zn was enriched in $PM_{2.5}$, showing a serious $PM_{2.5}$ pollution contributed from traffic and industrial emissions. Low concentrations of non-essential elements, which would be harmful to human body even at very low dose, including Ni, Cd, As, and Cr, were observed in this study [35].

Table 1. Concentrations of eleven elements in $PM_{2.5}$ during winter and summer in Xi'an (Unit: ng m^{-3}).

Elements	Winter (n = 16)		Summer (n = 15)		Annual Average
	Range	Average	Range	Average	
As	48–523	207 ± 202	8–55	42 ± 8	127 ± 160
Cd	2–16	9 ± 4	2–16	6 ± 4	8 ± 4
Cr	91–348	161 ± 95	64–405	142 ± 114	152 ± 103
Fe	1122–7129	2086 ± 1.399	251–1932	1368 ± 251	1739 ± 1068
K	2672–8227	4837 ± 1.663	887–4160	2388 ± 887	3570 ± 1800
Mn	7–243	121 ± 44	25–148	67 ± 25	95 ± 45
Mo	27–49	35 ± 7	3–33	27 ± 3	31 ± 7
Pb	266–1189	595 ± 278	80–436	208 ± 80	408 ± 283
Ni	14–29	18 ± 4	6–29	20 ± 6	19 ± 5
Zn	806–5301	1958 ± 1297	712–3304	1593 ± 712	1775 ± 1044
Cu	12–187	55 ± 52	1–81	26 ± 29	41 ± 21

Except for Ni, a consistent trend was observed in that the elemental mass concentrations in winter were higher than those in summer. This was especially notable for As, where the winter level was almost five times that of the summer level. This could be a result of domestic heating in winter of Xi'an. As is an important marker of coal combustion and a main emission pollutant from coal-fired power plants [21]. The power plant and the smelter near the sampling site also contribute to the high concentration of As [36]. Additionally, less precipitation, lower temperature, and calm weather, which are disadvantageous for the dilution and diffusion of air pollutants, may lead to thermal inversion and haze in Xi'an winter. The washing effect of rain is obvious for PM, so the air pollution level of elements in $PM_{2.5}$ was much lower in the rainy summer in Xi'an [37]. The average temperature was 1.1 °C, and the average precipitation was 8.9 mm in winter; in summer, the values were 29.3 °C and 76.9 mm, respectively [38].

3.2. The Source of Elements

The enrichment factors (EFs) of eleven elements are shown in Figure 2. Elements measured in this study were divided into two groups according to EFs: one was anthropogenic source elements (influenced little by natural sources), such as As, Cd, Cr, Mo, Pb, Zn, and Cu, with much higher EFs than 5; the second group with EFs below 5 (K and Mn) suggested that these elements were mainly influenced by natural sources.

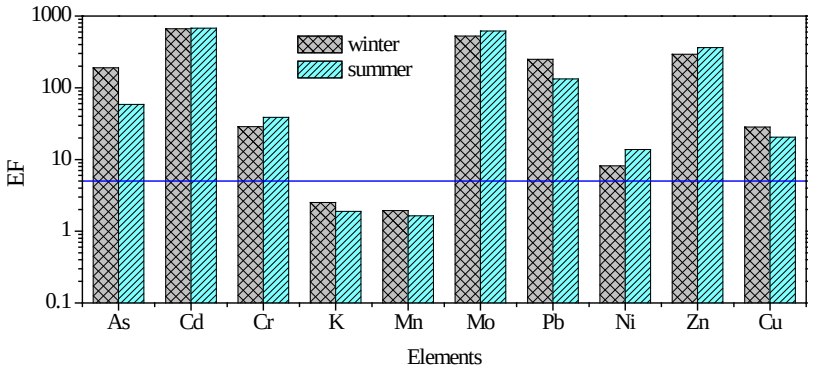

Figure 2. Elemental enrichment factors (EFs) relative to UCC (Earth's upper continental crust, [22]) for elements in $PM_{2.5}$ (particles with an equivalent diameter equal to or below 2.5 μm) over Xi'an during winter and summer.

The relative contributions of anthropogenic sources to the elemental concentrations are shown in Table 2. The mass concentrations of As, Mn, and Pb from anthropogenic sources in winter were significantly higher than those in summer. As and Pb are typical markers of coal combustion [39], and K is an effective indicator of biomass burning, as mentioned above. In addition, concentrations of Cd, Cr, Ni, Zn, and Cu were similar between summer and winter, indicating that emission sources of these elements did not obviously change with season. They may be produced from industry or traffic [40].

Table 2. The relative contributions of natural and anthropogenic sources to elements found in $PM_{2.5}$.

Elements	Summer			Winter		
	Anthropogenic Source (ng m^{-3})	Natural Source (ng m^{-3})	Anthropogenic Source Percentage (%)	Anthropogenic Source (ng m^{-3})	Natural Source (ng m^{-3})	Anthropogenic Source Percentage (%)
As	30	10	75.13	180	20	88.47
Cd	10	0.008	99.82	10	0.014	99.85
Cr	170	10	92.24	120	20	87.93
K	1130	1260	47.12	2910	1930	60.20
Mn	30	40.9	38.91	60	60	48.43
Mo	30	0.044	99.83	30	0.067	99.81
Pb	210	20	91.25	590	2.39	99.60
Ni	240	50	81.76	290	60	81.83
Zn	1590	4.38	99.73	1950	6.69	99.66
Cu	20	1.65	93.66	50	2.52	95.43

3.3. Comparison with Other Cities and Standard

Comparisons of elemental concentrations in $PM_{2.5}$ in Xi'an and other cities over the world are summarized in Table 3. The concentrations of elements in $PM_{2.5}$ in this study were higher than those in some Chinese cities and in other foreign cities. For example, Mn and Ni exhibited lower levels than those in Guangzhou and Baoshan, Shanghai in summer. The concentration of As in winter and Zn levels in both seasons in Xi'an were 5 to 10 times higher than those in other cities mentioned in Table 3. The concentration of Cd in Xi'an was higher than that in Yinchuan, Shanghai, and Taiwan, but much lower than that in the southern California. In addition, the concentration of Cr in Xi'an was significantly high, which may be associated with the electroplating factories in the suburb area of Xi'an [41]. The level of Pb in Xi'an was comparable to that in Guangzhou and Beijing, 2 to 4 times of that in Baoshan district, Shanghai, and as much as 10 times of that in southern California and New York. The K concentration in Xi'an was similar to Guangzhou, but higher than in foreign cities (Menen and southern California), which indicated that biomass burning was one of the main air pollution sources in Xi'an, and also in China in general. Crustal elements, Mn and Fe, in Xi'an showed higher concentrations than those in other areas except in the Northwestern city of Yinchuan. Generally, the pollution level of metal elements in Xi'an $PM_{2.5}$ was similar to that of Changsha and Guangzhou, but the pollutant concentration was slightly higher than other cities mentioned in Table 3.

In comparing the element concentrations with the latest China national ambient air quality standard [42], the concentration of As in $PM_{2.5}$ in Xi'an distinctly exceeded the standard (100%). This was mainly caused by coal combustion. The concentrations of Cd concentrations and Pb concentrations exceed the national standard by 80% and 43.8%, respectively. Therefore, this study confirmed severe pollution of several elements in $PM_{2.5}$ in Xi'an, especially As and heavy metals, and suggested that there should be reasonable concern for human health status and exposure to As and heavy metals in Xi'an, China.

Table 3. Comparison of eleven elements concentrations measured in $PM_{2.5}$ in this study and in other sites (Unit: ng m^{-3}).

Cities	Type	As	Cd	Cr	Fe	K	Mn	Mo	Pb	Ni	Zn	Cu	Reference
Xi'an	winter	207	9	161	2086	4837	121	35	595	18	1958	55	This study
	summer	42	6	142	1368	2388	67	27	208	20	1593	26	
Changsha			41						800		952	1109	[43]
Beijing							98		310		490	50	[44]
Guangzhou		40		4	873	3872	75		476	49	644	63	[37]
Yinchuan	winter		5	15	6360		139		191		254	15	[45]
	summer		4	19	7300		183		66		148	3	
Shanghai	Baoshan	32	5	58	1187		113		149	61	681	54	[7]
	Putuo	28	4	15	950		51		143	42	349	29	
	Huangpu	36	2	19	682		48		75	31	344	33	
	Jiading	27	2	17	666		29		67	32	300	26	
Taiwan			4	34	162		19		283		177	11	[46]
New York, USA			0	4	160				8		29	9	[47]
Milan, Italy				6	310		25		150		170		[40]
Barcelona, Spain				6	260		14		120		160	32	[48]
Southern California, USA			33	11	553	213	14	0.050	39	113	26		[49]
Menen, Belgium	winter			2	170	210	12		54	5	99	11	[50]
	summer			1	90	100	5		21	4	40	10	

3.4. Health Risk Assessment of Elements in $PM_{2.5}$

The exposure daily doses of eight elements by different exposure methods are calculated in Table 4. 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 each exposure pathway [46]. For non-cancer risk, the descending order of elements average daily exposure dose was Zn, Pb, As, Cr, Mn, Cu, Ni, and Cd for any exposure method. For cancer risk, the lifetime average daily doses (LADD) trend was As > Cr > Ni > Cd (Table 5).

Table 4. Average daily dose of each element from different exposure pathways: D_{ing}, ingestion; D_{inh}, inhalation; D_{dermal}, dermal contact (Unit: mg kg^{-1} day^{-1}).

Elements	D_{ing} (mg kg^{-1} day^{-1})		D_{inh} (mg kg^{-1} day^{-1})		D_{derm} (mg kg^{-1} day^{-1})	
	Adults	**Children**	**Adults**	**Children**	**Adults**	**Children**
As	2.70×10^{-3}	2.16×10^{-2}	4.10×10^{-7}	8.72×10^{-7}	8.23×10^{-6}	3.89×10^{-5}
Cd	8.81×10^{-5}	7.05×10^{-4}	1.33×10^{-8}	2.84×10^{-8}	2.68×10^{-7}	1.27×10^{-6}
Cr	1.61×10^{-3}	1.29×10^{-2}	2.45×10^{-7}	5.21×10^{-7}	4.92×10^{-6}	2.33×10^{-5}
Mn	1.60×10^{-3}	1.28×10^{-2}	2.42×10^{-7}	5.16×10^{-7}	4.87×10^{-6}	2.30×10^{-5}
Pb	4.49×10^{-3}	3.59×10^{-2}	6.81×10^{-7}	1.45×10^{-6}	1.37×10^{-5}	6.47×10^{-5}
Ni	2.97×10^{-4}	2.37×10^{-3}	4.50×10^{-8}	9.57×10^{-8}	9.04×10^{-7}	4.27×10^{-6}
Zn	2.07×10^{-2}	1.66×10^{-1}	3.14×10^{-6}	6.68×10^{-6}	6.31×10^{-5}	2.98×10^{-4}
Cu	7.48×10^{-4}	5.99×10^{-3}	1.13×10^{-7}	2.41×10^{-7}	2.28×10^{-6}	1.08×10^{-5}

Table 5. The lifetime average daily dose (LADD) of cancer elements via inhalation pathway (Unit: mg kg^{-1} day^{-1}).

Elements	LADD (mg kg^{-1} day^{-1})
As	2.29×10^{-7}
Cd	7.46×10^{-9}
Cr	1.37×10^{-7}
Ni	2.51×10^{-8}

The non-cancer risk assessments of adults and children for elements in $PM_{2.5}$ by three pathways are listed in Table 6. The descending order of single element non-cancer risk was as follows: As, Pb, Cr, Cd, Zn, Mn, Cu, and Ni for ingestion; the order was Mn, Cr, As, Pb, Cd, Zn, Cu, and Ni for inhalation; and As, Pb, Cr, Cd, Mn, Cu, Zn, and Ni for dermal contact. Moreover, separating the three main exposure routes, for all eight elements, non-cancers risks from ingestion (10.8 for adults and 86.7 for children) and dermal contact (0.12 for adults and 0.58 for children) are much greater compared to inhalation exposure (0.027 and 0.056 for adults and children) (Table 6). Except for As, Pb, and Cr (children), HIs of other elements were much lower than 1, indicating that the non-cancer risk was controlled within the safe limit [28]. Coupled with the concentrations of elements in $PM_{2.5}$ in Xi'an in Table 1, As, Pb, and Cr showed lower concentration levels but higher non-cancer risks [51]. Therefore, it is imperative to strengthen air pollution control and air quality management in Xi'an, especially in regard to As, Pb, and Cr related emission sources.

Table 6. Non-cancer risks for each element via three exposure pathways. HQ, hazard quotient; HI, hazard index.

Elements	HQ_{ing}		HQ_{inh}		HQ_{dermal}		HI	
	Adults	Children	Adults	Children	Adults	Children	Adults	Children
As	9.01	7.21×10^{1}	1.02×10^{-3}	3.22×10^{-3}	6.69×10^{-2}	3.16×10^{-1}	9.08	72.41
Cd	8.81×10^{-2}	7.05×10^{-1}	4.45×10^{-5}	9.47×10^{-5}	5.37×10^{-3}	2.54×10^{-2}	0.09	0.73
Cr	3.23×10^{-1}	2.58	8.55×10^{-3}	1.82×10^{-2}	1.97×10^{-2}	9.30×10^{-2}	0.35	2.69
Mn	3.40×10^{-2}	2.72×10^{-1}	1.73×10^{-2}	3.69×10^{-2}	2.03×10^{-3}	9.60×10^{-3}	0.05	0.32
Pb	1.28	1.03×10^{1}	1.93×10^{-4}	4.12×10^{-4}	2.61×10^{-2}	1.23×10^{-1}	1.31	10.39
Ni	1.48×10^{-2}	1.19×10^{-1}	2.18×10^{-6}	4.65×10^{-6}	9.04×10^{-4}	4.27×10^{-3}	0.02	0.12
Zn	6.91×10^{-2}	5.52×10^{-1}	7.13×10^{-6}	9.27×10^{-6}	1.05×10^{-3}	4.97×10^{-3}	0.07	0.56
Cu	2.02×10^{-2}	1.62×10^{-1}	2.82×10^{-6}	6.00×10^{-6}	1.20×10^{-3}	5.67×10^{-3}	0.02	0.17
Total	1.08×10^{1}	8.67×10^{1}	2.71×10^{-2}	5.56×10^{-2}	1.23×10^{-1}	5.83×10^{-1}	10.99	87.39

Based on assessments of non-cancer and cancer risks (ILCRs) for elements in Figure 3, the highest threat of non-cancer risk to the human body was As, followed by Pb. The average non-cancer risks of As and Pb for children both were approximately 8 times of adults. Therefore, this indicated that children were more sensitive to non-cancer effects of $PM_{2.5}$ elements [13] and we should minimize exposure to As, Pb, and Cr sources, especially for children. The decreased cancer risks occur in the following order of Cr, As, Cd, and Ni in Xi'an $PM_{2.5}$. The values of As and Cr were higher than 10^{-6}, indicating that the $PM_{2.5}$ in Xi'an had cancer risk to the residents in this study. Even so, we must pay attention to carcinogenic As and Cr in Xi'an, which still are concerns to the residents.

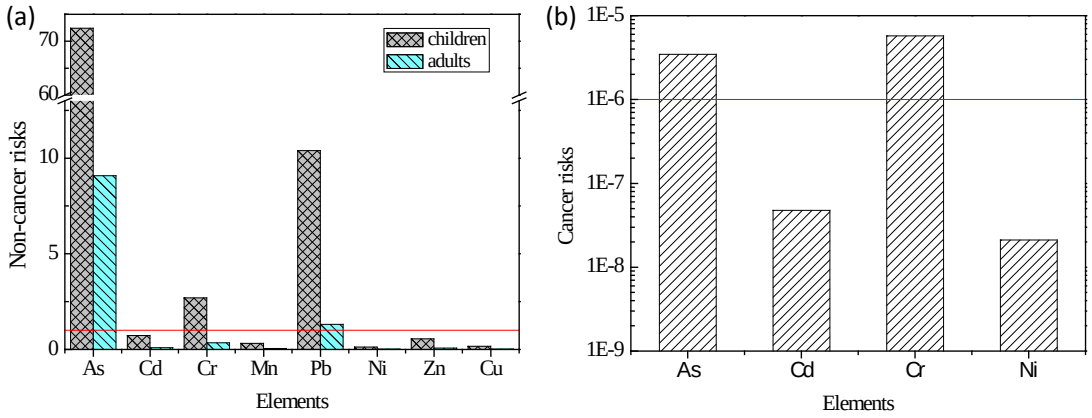

Figure 3. Non-cancer (**a**) and cancer risks (**b**) for elements in $PM_{2.5}$ (red lines represent the threshold values for non-cancer and cancer risks).

4. Conclusions

Eleven elements (As, Cd, Cr, Fe, K, Mn, Mo, Pb, Ni, Zn, and Cu) in $PM_{2.5}$ of Xi'an were investigated in summer and winter. The Pb, Cd, and As concentrations exceeded AAQS (Ambient Air Quality Standard) in China, especially As. Mass concentrations of elements in winter were much higher than those in summer, with the exception of Ni. Seasonal variations of As, Pb, and K were observed obviously due to extra coal and biomass burning in winter for domestic heating. The EFs of As, Cd, Pb, Mo, Zn, Cr, and Cu were more than 5, with the highest value for Cd, pointing out relatively higher contributions from anthropogenic sources. Elemental pollution in $PM_{2.5}$ in Xi'an was serious compared with other cities.

Average daily exposure doses for children were higher than those for adults for each exposure pathway. The average daily exposure dose occurred in the following decreasing order: Zn, Pb, As, Cr, Mn, Cu, Ni, and Cd for non-cancer risk, while the order was As, Cr, Ni, and Cd for cancer risk. The non-cancer risk of As and Pb were much more than 1 for both children and adults, demonstrating

that As and Pb emissions should be controlled effectively in Xi'an. The ILCR of As and Cr were higher than 10^{-6}, indicating that cancer risk from elements in $PM_{2.5}$ should be a concern in Xi'an. Further studies should be conducted to investigate exposure parameters specifically for Chinese residents and air pollution transportation factors in order to reduce the health risk assessment uncertainties in China.

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