

Article

# Sources and Health Risks of Heavy Metals in PM<sub>2.5</sub> in a Campus in a Typical Suburb Area of Taiyuan, North China

Kankan Liu \* , Qingmin Shang and Changyuan Wan

School of Environment and Safety Engineering, North University of China, Taiyuan 030051, China; cloud6@foxmail.com (Q.S.); wanchangyuan@163.com (C.W.)

\* Correspondence: liukkcn@139.com

Received: 27 December 2017; Accepted: 30 January 2018; Published: 2 February 2018

**Abstract:** To evaluate air pollution and the public health burden of heavy metals in PM<sub>2.5</sub> in a campus with a population of approximately 40,000 in a typical suburb area of Taiyuan, North China, PM<sub>2.5</sub> measurements were conducted during the spring and winter of 2016. The average concentrations of PM<sub>2.5</sub> in spring and winter were  $97.3 \pm 35.2 \mu\text{g m}^{-3}$  and  $205.9 \pm 91.3 \mu\text{g m}^{-3}$ , respectively. The order of concentration of heavy metals in PM<sub>2.5</sub> was as follows: Zn > Pb > Mn > Cu > Cr > Ni > Cd > As, in both spring and winter. The concentrations of Cd and Pb in winter and the concentrations of Cr in both spring and winter in this study were significantly higher than the corresponding air quality standard values. Road/soil dust, industrial emissions/coal combustion, and vehicle emissions/oil combustion and coal combustion/industrial emissions, road/soil dust, and vehicle emissions/oil combustion were identified by principal component analysis to be the major sources of heavy metals for spring and winter, respectively. The carcinogenic risks posed by Cr via the three exposure pathways (except for inhalation exposure to children) and by Pb via ingestion exposure exceeded the acceptable level for both children and adults. The non-carcinogenic risks posed by Mn via inhalation for both children and adults, and by Cr and Pb for children via ingestion exceeded the acceptable level.

**Keywords:** heavy metals; PM<sub>2.5</sub>; health risk; campus

## 1. Introduction

Severe haze pollution, mainly caused by fine particulate matters with aerodynamic diameters less than 2.5  $\mu\text{m}$  (PM<sub>2.5</sub>), is becoming one of the hottest issues in recent years [1–3]. PM<sub>2.5</sub> not only affects the air visibility by light extinction [4,5], but also plays an important role in being harmful to human health [6], mainly because it can carry varieties of pathogenic components (e.g., viruses, polycyclic aromatic hydrocarbons, bacteria, and heavy metals) and can enter the respiratory system or other organs of human beings [7]. Epidemiologic evidence associated cognitive deficits with PM<sub>2.5</sub> exposure among the elderly [8]. Cacciottolo et al. conducted time-to-event analyses to examine associations between long-term residential exposure to PM<sub>2.5</sub> and adverse neurocognitive outcomes, and found that residing in places with fine particles exceeding United States Environmental Protection Agency (US EPA) standards increased the risks for global cognitive decline and all-cause dementia, respectively, by 81% and 92% [9]. Heavy metals (e.g., Cr, Mn, Ni, Cu, Zn, As, Cd, and Pb) have been used by humans for thousands of years. Previous studies have demonstrated the adverse health effect relationship between particulate matter exposure and toxic heavy metals [10–13]. The International Agency for Research on Cancer (IARC) classified As, Ni, Cd, and Cr as class I carcinogenic contaminants. Human beings exposed to As via drinking water show excess risk of mortality due to lung, bladder, and kidney cancer, with the risk increasing with increasing exposure. In addition, those exposed to

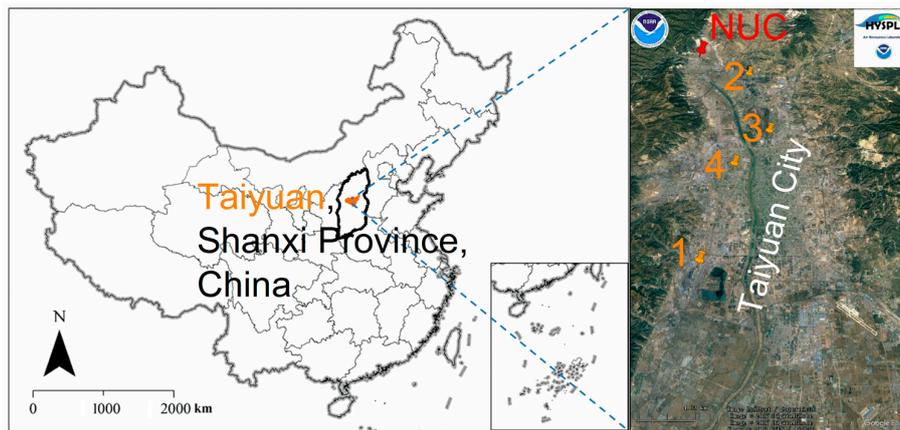
As by inhalation, such as smelter workers, pesticide manufacturers, and miners in many different countries, consistently demonstrate an excess risk of lung cancer [14]. Cd exposure was reported to be related to chronic renal failure [15]. Pb inorganics were classified as class II(B) carcinogens (i.e., 'possible human carcinogen'). The risks of spontaneous abortion, reduced fetal growth (preterm delivery, low birth weight), and reduced offspring neurobehavioral development may be related with high levels of parental Pb exposure [16]. Although Zn, Cu, and Mn were classified as non-carcinogenic contaminants, Zn, for example, as the major heavy metal in airborne PM<sub>2.5</sub>, may cause damage to plasmid DNA [17].

University campuses usually have high population densities. The populations on university campuses are mainly composed of students and teachers. There are usually also kindergarten, elementary, and secondary schools on campus. Students leave campus for a specific period each year. Some studies on PM<sub>2.5</sub> have been conducted on campuses; however, most of those campuses are in the inner city. North University of China (NUC), with a population of approximately 40,000 (students and teachers), is located in a typical suburb area in the north of Taiyuan, surrounded by villages. Most of the faculty's children in the surrounding villages also study on the campus. The local residents mainly depend on student-related business for their livelihood (e.g., illegal taxis, restaurants with raw-coal burning for energy), and columns of acrid black smoke bloom upward from chimneys of the farmers' coal stoves in winter. The distance from the campus to the center of Taiyuan City is about 25 km. The aim of the present study is to evaluate air pollution and the public health burden of heavy metals in PM<sub>2.5</sub> in the NUC campus. PM<sub>2.5</sub> measurements were conducted during the spring and winter of 2016. Eight heavy metals (i.e., Cr, Mn, Ni, Cu, Zn, As, Cd, and Pb) in PM<sub>2.5</sub> were quantified and source-identified. Additionally, the health risks of exposure to the observed elements in particulate matter were assessed for both the children and adults on the campus.

## 2. Experiments

### 2.1. Sample Collection and Analysis

The sampling site in this study was the rooftop of a science building (about 27 m above ground level; 38.02 N, 112.45 E) of NUC in a typical suburb area in the north of Taiyuan City, with villages around. Taiyuan City and its main power plants and industrial facilities have been described in detail in our previous study [18]. The specific locations of the sampling site, power plants, and industrial facilities are shown in Figure 1. The methods of sample collection and analysis have also been described in detail in our previous study [18]. Shortly, PM<sub>2.5</sub> were collected on prebaked (600 °C, 4 h) quartz microfiber filters (90 mm, Munktell Ahlstrom, Falun, Sweden) for 24 h (starting at approximately 8:00 a.m.) by a PM<sub>2.5</sub> sampler (KC-6120, Qingdao Laoshan Electronic Instrument Factory Co., Ltd., Qingdao, China) at a flow rate of 100 L min<sup>-1</sup>, and weighed by an electronic microbalance (FA1004, Lichen, Shanghai, China). The wind speeds and directions were monitored using an anemometer (ZCF-5, Sipeik, Hefei, China). Heavy metals (i.e., Cr, Mn, Ni, Cu, Zn, As, Cd, and Pb) were measured using an inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent 5100).



**Figure 1.** Sampling site and the main industries (NUC represents the sampling site at the North University of China; 1, 2, 3, and 4 are the First and Second Power Stations, Taiyuan Iron and Steel Factory, and Taiyuan Heavy Machinery Factory, respectively).

## 2.2. Health Risk Assessment

Because of the different effects on the respiratory systems and behaviors of residents living in this area, the subjects were divided into children and adults [19]. The daily dose through inhalation ( $D_{inh}$ ,  $\text{mg kg}^{-1} \text{ day}^{-1}$ ), ingestion ( $D_{ing}$ ,  $\text{mg kg}^{-1} \text{ day}^{-1}$ ), and dermal contact ( $D_{der}$ ,  $\text{mg kg}^{-1} \text{ day}^{-1}$ ) were calculated using Equations (1)–(3) [20,21].

$$D_{inh} = \frac{C \times \text{InhR} \times \text{ED} \times \text{EF}}{\text{BW} \times \text{AT}} \quad (1)$$

$$D_{ing} = \frac{C \times \text{IngR} \times \text{ED} \times \text{EF}}{\text{BW} \times \text{AT}} \times 10^6 \quad (2)$$

$$D_{der} = \frac{C \times \text{SA} \times \text{AF} \times \text{ABS} \times \text{ED} \times \text{EF}}{\text{BW} \times \text{AT}} \times 10^6 \quad (3)$$

All parameters above are described in Table 1. The concentrations units of elements were transformed from  $\mu\text{g m}^{-3}$  to  $\text{mg kg}^{-1}$  before conducting the risk assessment posed by heavy metals in  $\text{PM}_{2.5}$  via injection and dermal. The upper limit of the 95% confidence interval for the mean (95% UCL) was calculated to represent the “reasonable maximum exposure” [19] in an exposure assessment, as shown in the following formula [19,20]:

$$C_{95\%UCL} = \exp \left\{ \bar{X} + 0.5 \times s^2 + \frac{S \times H}{\sqrt{n-1}} \right\} \quad (4)$$

where  $\bar{X}$  is the arithmetic mean of the log-transformed data,  $s$  is the standard deviation of the log-transformed data,  $H$  is the  $H$ -statistic, and  $n$  is the number of samples. Because of the differences in the body size between Chinese and foreigners, the values representing exposed skin area adopted here were  $2011.25 \text{ cm}^2$  for adults and  $1077.5 \text{ cm}^2$  for children, according to Reference [22]. The dermal absorption factor (ABS) for As, Cd, and others were 0.03, 0.001 [19,20,23,24], and 0.01 [19], respectively.

**Table 1.** Exposure factors for health risk assessment model.

Parameters	Definition	Values		References
		Children	Adult	
C ( $\mu\text{g m}^{-3}$ or $\text{mg kg}^{-1}$ )	Concentrations of elements	95% UCL	95% UCL	This study
InhR ( $\text{m}^3 \text{day}^{-1}$ )	Inhalation rate	7.6	20	[20]
ED (year)	Exposure duration	6	24	[19,20]
EF ( $\text{days year}^{-1}$ )	Exposure frequency	180	180	This study
BW (kg)	Body weight	15	70	[19]
AT (day)	Average exposure time			
(for non-carcinogenic)		ED $\times$ 365	ED $\times$ 365	[20]
(for carcinogenic)		70 $\times$ 365	70 $\times$ 365	[20]
IngR ( $\text{mg day}^{-1}$ )	Ingestion rate	200	100	[19,24]
SA ( $\text{cm}^2$ )	Exposed skin area	1077.5	2011.25	[22]
SL ( $\text{mg cm}^{-2} \text{day}^{-1}$ )	Skin adherence factor	0.2	0.07	[19,20]
ABS	Dermal absorption factor	As (0.03)	As (0.03)	[19,23,25]
		Cd (0.001)	Cd (0.001)	[19,23,24]
		Others (0.01)	Others (0.01)	[19]

The hazard quotient (HQ) is used for assessing the level of concern for each non-carcinogenic contaminant, and the hazard index (HI) is the sum of the HQs for several chemicals. If the HQ or HI equals or exceeds one, there may be concern for potential exposure to site contaminants. Lifetime cancer risk (CR) was used to assess carcinogenic risk, and the acceptable or tolerable risk is  $1 \times 10^{-6}$  to  $1 \times 10^{-4}$  [21]. Equations are as below [19,20,24]:

$$\text{HQ} = \text{D}/\text{RfD} \tag{5}$$

$$\text{HI} = \sum \text{HQ} \tag{6}$$

$$\text{CR} = \text{D}_{\text{inh}} \times \text{IUR} = \text{D}_{\text{ing}} \times \text{SF} = \text{D}_{\text{der}} \times (\text{SF}/\text{G}) \tag{7}$$

where RfD refers to the reference dose of each intake path ( $\text{mg kg}^{-1} \text{day}^{-1}$ ); IUR is the inhalation unit risk ( $(\mu\text{g m}^{-3})^{-1}$ ); SF is the slope factor ( $\text{mg kg}^{-1} \text{d}^{-1}$ ); and G is the gastrointestinal absorption factor. The values of RfD, IUR, SF, and G for heavy metals are summarized in Table 2.

**Table 2.** The values of the reference dose (RfD;  $\text{mg kg}^{-1} \text{day}^{-1}$ ), inhalation unit risk (IUR;  $(\mu\text{g m}^{-3})^{-1}$ ), slope factor (SF;  $\text{mg kg}^{-1} \text{d}^{-1}$ ), and gastrointestinal absorption factor (G) for heavy metals [19,23,24,26].

Parameters	Cr	Mn	Ni	Cu	Zn	As	Cd	Pb
RfD								
Inhalation	$1.00 \times 10^{-4}$	$5.00 \times 10^{-5}$	$5.00 \times 10^{-5}$			$1.50 \times 10^{-5}$	$1.00 \times 10^{-5}$	
Ingestion	$3.00 \times 10^{-3}$	$1.40 \times 10^{-1}$	$5.00 \times 10^{-2}$	$4.00 \times 10^{-2}$	$3.00 \times 10^{-1}$	$3.00 \times 10^{-4}$	$1.00 \times 10^{-3}$	$3.50 \times 10^{-3}$
Dermal	$2.50 \times 10^{-2}$	$1.00 \times 10^0$	$4.00 \times 10^{-2}$	$1.00 \times 10^0$	$1.00 \times 10^0$	$1.00 \times 10^0$	$2.50 \times 10^{-2}$	$1.00 \times 10^0$
IUR	$1.20 \times 10^{-2}$	/	$2.40 \times 10^{-4}$	/	/	$4.30 \times 10^{-3}$	$1.80 \times 10^{-3}$	$8.00 \times 10^{-5}$
SF	$5.00 \times 10^{-1}$	/	$8.40 \times 10^{-2}$	/	/	$1.50 \times 10^0$	$6.40 \times 10^{-1}$	$2.80 \times 10^{-1}$
G	$2.50 \times 10^{-2}$	/	$4.00 \times 10^{-2}$	/	/	$1.00 \times 10^0$	$2.50 \times 10^{-2}$	$1.00 \times 10^0$

### 3. Results and Discussion

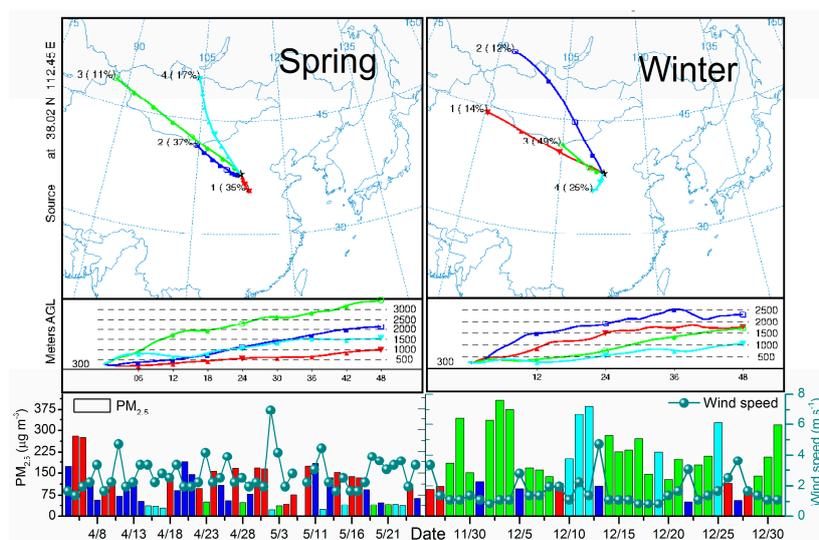
#### 3.1. The Characteristics of Heavy Metals in $\text{PM}_{2.5}$

The measured concentrations of  $\text{PM}_{2.5}$  and eight heavy metals are presented in Table 3. The average concentrations of  $\text{PM}_{2.5}$  in the spring ( $97.3 \pm 35.2 \mu\text{g m}^{-3}$ ) and winter ( $205.9 \pm 91.3 \mu\text{g m}^{-3}$ ) were 2.9 and 5.9 times higher than the daily air quality limit ( $35 \mu\text{g m}^{-3}$  in standard I) set by the Ministry of Environmental Protection of China (MEPC).  $\text{PM}_{2.5}$  concentrations for more than 94% of the sampling days exceeded  $35 \mu\text{g m}^{-3}$ , and even exceeded  $75 \mu\text{g m}^{-3}$  (standard II set by the MEPC) on more than 82% of the sampling days.

**Table 3.** The average concentrations (mean  $\pm$  SD) of PM<sub>2.5</sub> ( $\mu\text{g m}^{-3}$ ) and heavy metals (ng m<sup>-3</sup>) at NUC and in other cities of China.

Species	NUC		Beijing	Shanghai	Taichung	Nanjing	Guangzhou	Foshan
	Spring (n = 48)	Winter (n = 37)	Winter [27]	Winter [28]	Annual [29]	September [19]	[30]	Winter [31]
PM <sub>2.5</sub>	97.3 $\pm$ 35.2	205.9 $\pm$ 91.3	126	75.89	42.8 $\pm$ 17.4	/	91.4 $\pm$ 21	136.4 $\pm$ 40.5
Cr	63.6 $\pm$ 45.6	105.0 $\pm$ 80.8	30	7	33.5 $\pm$ 48	22.5 $\pm$ 7.8	51 $\pm$ 11	/
Mn	171.9 $\pm$ 64.8	166.5 $\pm$ 78.8	70	62	19.1 $\pm$ 20.5	48.3 $\pm$ 6.4	39 $\pm$ 8	200.6 $\pm$ 129.4
Ni	25.3 $\pm$ 18.9	38.8 $\pm$ 30.8	40	6	11.8 $\pm$ 29.9	6.7 $\pm$ 3.7	33 $\pm$ 7	/
Cu	83.1 $\pm$ 48.3	115.6 $\pm$ 52.8	200	13	11.5 $\pm$ 19.9	65.7 $\pm$ 32.1	109 $\pm$ 23	283.8 $\pm$ 174.7
Zn	338.2 $\pm$ 147.8	554.0 $\pm$ 161.6	310	235	177.8 $\pm$ 103.0	230 $\pm$ 69.3	680 $\pm$ 146	2214 $\pm$ 1438
As	1.8 $\pm$ 1.1	5.5 $\pm$ 3.5	10	/	/	4.3 $\pm$ 2.3	81 $\pm$ 17	76.6 $\pm$ 49.1
Cd	2.8 $\pm$ 0.3	10.7 $\pm$ 2.4	0	1	4.3 $\pm$ 8.5	1.3 $\pm$ 0.1	14 $\pm$ 3	42.6 $\pm$ 45.2
Pb	214.3 $\pm$ 109.0	517.1 $\pm$ 185.3	150	64	283.1 $\pm$ 252.9	81.5 $\pm$ 12.0	373 $\pm$ 80	675.7 $\pm$ 378.5

As listed in Table 3, Zn and Pb were the most abundant metals in PM<sub>2.5</sub> in both the spring and winter. The order of concentrations of heavy metals in PM<sub>2.5</sub> were as follows: Zn > Pb > Mn > Cu > Cr > Ni > Cd > As, in both the spring and winter. The concentrations of Cr, Ni, Cu, Zn, As, Cd, and Pb were 1.65, 1.53, 1.39, 1.64, 3.06, 3.82, and 2.41 times higher in winter than in spring, respectively. However, the concentration of Mn was slightly higher in spring than in winter, which should be ascribed to the frequent dust storms in spring. Previously studies have shown that Mn was the main pollutant in soil and street dust [32,33], especially in Asian natural soil dust [32,34,35]. Therefore, Mn is usually a marker of particulate matter originating soil and re-suspension dust [36]. According to MEPC (GB3095-2012), the annual average concentration standards of Cr(VI), As, Cd, and Pb are 0.025, 6, 5, and 500 ng m<sup>-3</sup>, respectively. The concentrations of Cr, Cd, and Pb in winter in this study were significantly higher than the standard values. The concentration of Cr in spring also exceeded the standard value. Considering that the toxicity of Cr is dependent on its valence states [19] and the concentration ratio of Cr(VI) and Cr(III) is about 1 to 6 [37], the concentrations of Cr in this study were still higher. The concentration of As in both the spring and winter were lower than the corresponding standard value and the values reported in other cities [27,28,31]. The concentrations of most of heavy metals in PM<sub>2.5</sub> in this work were lower than those in Foshan [31], but much higher than those in Beijing [27], Shanghai [28], Nanjing [19], and Taichung [29]. The 48-h back trajectories starting at 300 m from NUC were computed by using the HYSPLIT 4 model of the National Oceanic and Atmospheric Administration (NOAA) (<https://ready.arl.noaa.gov/HYSPLIT.php>). As shown in Figure 2, the major pollution episodes usually occurred during periods with air parcels originating from the southeast and southwest for spring and winter, respectively, and from northwest directions with slow wind speed.

**Figure 2.** The back trajectory cluster analysis and corresponding PM<sub>2.5</sub> concentrations and wind speeds at NUC during the spring and the winter of 2016.

### 3.2. Source Identification

IBM SPSS (version 22) was employed for the principal component analysis (PCA). Table 4 shows the principal component loadings of the heavy metals during the study periods with corresponding variances. The PCA results demonstrated that 86.64% and 92.76% of the data variance for the spring and winter can be explained by three factors, respectively.

**Table 4.** Principal component analysis (PCA) results of heavy metals in PM<sub>2.5</sub> at NUC.

Heavy Metals	Spring			Winter		
	FI	FII	FIII	FI	FII	FIII
Cr	0.891			0.753	0.458	
Mn	0.925			0.478	0.920	
Ni		0.856	0.263	0.935		
Cu	0.699	0.249		0.787	0.415	0.320
Zn	0.761	0.534		0.215	0.614	0.476
As	0.672	0.414	0.409	0.819	0.219	
Cd			0.952			0.985
Pb	0.407	0.781	0.243	0.948		0.207
Variance (%)	49.47	23.86	13.31	56.59	21.91	14.26

In spring, 49.47% of the total variance of the data can be explained by factor I (FI), with high loadings of Mn (0.925), Cr (0.891), Zn (0.761), Cu (0.699), As (0.672), and Pb (0.407). Mn was considered as a marker of re-suspension and soil dust [32–34,36,38]. North China frequently suffered from dust storms in spring [2]. This factor should be well associated with dust (Mn, Cr) re-suspended from roads and soil [32,33,36,38]. Factor II (FII) is dominated by Ni (0.856), Pb (0.781), and moderately associated with Zn (0.534) and As (0.414), which has been reported to mainly originate from industrial emissions and coal combustion [32,33,38–40]. Factor III (FIII) is dominated by Cd (0.856), which originated from vehicle emissions/oil combustion [32].

In winter, FI (56.59%) has high loadings for Pb (0.948), Ni (0.935), Cr (0.753), Cu (0.787), and As (0.819). This may be mainly due to coal combustion (Pb, As, Zn) for heating (including central-heating, domestic coal-stove-heating) and industry and industrial emissions (As, Ni, Cd, Cu) [32,33,38,39,41–43]. FII shows the high loading of Mn (0.920), with moderate loadings of Zn (0.614), Cr (0.458), and Cu (0.415), which should be well associated with dust re-suspended from roads and soil. [32,36,38,39]. FIII, which explains 14.26% of the total variance, has high loadings of Cd (0.985). Vehicle emissions and oil combustion should be responsible for this source [40,43–45].

### 3.3. Health Risk Assessment

In order to evaluate the threat to the health of the local students, teachers, and inhabitants caused by heavy metals in PM<sub>2.5</sub>, the carcinogenic and non-carcinogenic risks for both children and adults via direct inhalation, ingestion, and dermal contact were assessed and are aggregated in Table 5. For the carcinogenic risks, direct ingestion appeared to be the main exposure pathway for both children and adults, followed by dermal contact and then inhalation exposure for children, and inhalation exposure and then dermal contact for adults. Except for inhalation exposure to children, the carcinogenic risks posed by Cr via the three exposure pathways exceeded the acceptable level ( $1 \times 10^{-4}$ ) for both children and adults. The carcinogenic risks posed by Pb via ingestion exposure also exceeded the acceptable level for both children and adults. The non-carcinogenic risks posed by Mn via inhalation for both children and adults and posed by Cr and Pb for children via ingestion were higher than 1. Only the sum of carcinogenic risks for children through inhalation exposure in the two sampling areas were within the threshold value ( $1 \times 10^{-4}$ ), and only the HI (the sum of HQs) for adults through dermal exposure was below 1, while the others all exceeded their threshold values. The results show that the health risks from heavy metals in PM<sub>2.5</sub> via the three exposure pathways to children and adults in

rural areas were consistent with those in urban areas, which also confirms that severe air pollution in suburb areas should be paid more attention. Therefore, cancer risk and non-carcinogenic risks to children and adults posed by heavy metals in PM<sub>2.5</sub> should not be neglected in these areas of Taiyuan given the present air quality.

**Table 5.** Carcinogenic and non-carcinogenic risks of each element for children and adults via inhalation, ingestion, and dermal exposure.

Heavy Metals	Carcinogenic (CR)		Non-Carcinogenic (HQ)	
	Children	Adults	Children	Adults
Inhalation exposure				
Cr	$7.27 \times 10^{-5}$	<b><math>2.91 \times 10^{-4}</math></b>	$1.44 \times 10^{-2}$	$1.44 \times 10^{-2}$
Mn			<b><math>2.28 \times 10^0</math></b>	<b><math>2.28 \times 10^0</math></b>
Ni	$4.78 \times 10^{-7}$	$1.91 \times 10^{-6}$	$4.64 \times 10^{-1}$	$4.64 \times 10^{-1}$
As	$7.83 \times 10^{-7}$	$3.13 \times 10^{-6}$	$1.42 \times 10^{-1}$	$1.42 \times 10^{-1}$
Cd	$4.53 \times 10^{-7}$	$1.81 \times 10^{-6}$	$2.93 \times 10^{-1}$	$2.93 \times 10^{-1}$
Pb	$1.70 \times 10^{-6}$	$6.79 \times 10^{-6}$		
Sum	$7.61 \times 10^{-5}$	<b><math>3.04 \times 10^{-4}</math></b>	<b><math>3.19 \times 10^0</math></b>	<b><math>3.19 \times 10^0</math></b>
Ingestion exposure				
Cr	<b><math>2.72 \times 10^{-4}</math></b>	<b><math>1.36 \times 10^{-4}</math></b>	<b><math>2.12 \times 10^0</math></b>	$2.65 \times 10^{-1}$
Mn			$7.31 \times 10^{-2}$	$9.14 \times 10^{-3}$
Ni	$1.50 \times 10^{-5}$	$7.52 \times 10^{-6}$	$4.18 \times 10^{-2}$	$5.22 \times 10^{-3}$
Cu			$1.44 \times 10^{-1}$	$1.80 \times 10^{-2}$
Zn			$7.26 \times 10^{-2}$	$9.07 \times 10^{-3}$
As	$2.48 \times 10^{-5}$	$1.24 \times 10^{-5}$	$6.38 \times 10^{-1}$	$7.97 \times 10^{-2}$
Cd	$1.45 \times 10^{-5}$	$7.24 \times 10^{-6}$	$3.64 \times 10^{-1}$	$3.30 \times 10^{-2}$
Pb	<b><math>5.35 \times 10^{-4}</math></b>	<b><math>2.67 \times 10^{-4}</math></b>	<b><math>6.37 \times 10^0</math></b>	$7.96 \times 10^{-1}$
Sum	<b><math>8.62 \times 10^{-4}</math></b>	<b><math>4.31 \times 10^{-4}</math></b>	<b><math>9.72 \times 10^0</math></b>	$1.21 \times 10^0$
Dermal exposure				
Cr	<b><math>1.17 \times 10^{-4}</math></b>	<b><math>2.19 \times 10^{-4}</math></b>	$9.13 \times 10^{-1}$	$4.26 \times 10^{-1}$
Mn			$7.88 \times 10^{-4}$	$3.36 \times 10^{-4}$
Ni	$4.05 \times 10^{-6}$	$7.56 \times 10^{-6}$	$1.13 \times 10^{-2}$	$5.25 \times 10^{-3}$
Cu			$1.55 \times 10^{-3}$	$7.25 \times 10^{-4}$
Zn			$7.82 \times 10^{-4}$	$3.65 \times 10^{-4}$
As	$8.00 \times 10^{-7}$	$1.49 \times 10^{-6}$	$2.06 \times 10^{-2}$	$9.62 \times 10^{-3}$
Cd	$6.24 \times 10^{-7}$	$1.17 \times 10^{-6}$	$1.14 \times 10^{-2}$	$5.31 \times 10^{-3}$
Pb	$5.76 \times 10^{-6}$	$1.08 \times 10^{-5}$	$6.86 \times 10^{-2}$	$3.20 \times 10^{-2}$
Sum	<b><math>1.29 \times 10^{-4}</math></b>	<b><math>2.40 \times 10^{-4}</math></b>	<b><math>1.03 \times 10^0</math></b>	$4.80 \times 10^{-1}$

Values in bold are those that exceeded their thresholds.

#### 4. Conclusions

In the study, PM<sub>2.5</sub> samples were collected from a campus with a population of approximately 40,000 in a typical suburb area of Taiyuan, North China. The average concentrations of PM<sub>2.5</sub> in spring and winter were  $97.3 \pm 35.2 \mu\text{g m}^{-3}$  and  $205.9 \pm 91.3 \mu\text{g m}^{-3}$ , respectively. The order of concentrations of heavy metals in PM<sub>2.5</sub> were as follows: Zn > Pb > Mn > Cu > Cr > Ni > Cd > As, in both spring and winter. PCA results indicated that the main sources of heavy metals in PM<sub>2.5</sub> were road/soil dust, industrial emissions/coal combustion, and vehicle emissions/oil combustion in the spring, and coal combustion/industrial emissions, road/soil dust, and vehicle emissions/oil combustion in the winter. For the carcinogenic risks, direct ingestion appeared to be the main exposure pathway for both children and adults. Except for inhalation exposure to children, the carcinogenic risks posed by Cr via the three exposure pathways exceeded the acceptable level ( $1 \times 10^{-4}$ ) for both children and adults. The carcinogenic risks posed by Pb via ingestion exposure also exceeded the acceptable level for both

children and adults. The non-carcinogenic risks posed by Mn via inhalation for both children and adults, and posed by Cr and Pb via ingestion for children exceeded the acceptable levels.

**Acknowledgments:** This work was financially supported by the Natural Science Foundation of Shanxi (201601D021135) and the Chinese National Natural Science Foundation (21707125).

**Author Contributions:** Kankan Liu conceived and designed the experiments. Kankan Liu and Qingmin Shang wrote the paper; Qingmin Shang and Changyuan Wan performed the experiments and analyzed the data.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Liu, P.; Zhang, C.; Mu, Y.; Liu, C.; Xue, C.; Ye, C. The possible contribution of the periodic emissions from farmers' activities in the North China Plain to atmospheric water-soluble ions in Beijing. *Atmos. Chem. Phys.* **2016**, *16*, 10097–10109. [[CrossRef](#)]
2. Liu, P.; Zhang, C.; Xue, C.; Mu, Y.; Liu, J.; Zhang, Y.; Tian, D. The contribution of residential coal combustion to atmospheric PM<sub>2.5</sub> in northern China during winter. *Atmos. Chem. Phys.* **2017**, *17*, 11503–11520. [[CrossRef](#)]
3. Zhang, R.; Jing, J.; Tao, J.; Hsu, S.C.; Wang, G.; Cao, J. Chemical characterization and source apportionment of PM<sub>2.5</sub> in Beijing: Seasonal perspective. *Atmos. Chem. Phys.* **2013**, *13*, 7053–7074. [[CrossRef](#)]
4. Buseck, P.R.; Posfai, M. Airborne minerals and related aerosol particles: Effects on climate and the environment. *Proc. Natl. Acad. Sci. USA* **1999**, *96*, 3372–3379. [[CrossRef](#)] [[PubMed](#)]
5. Cheng, Y.; Eichler, E.; Wiedensohler, A.; Heintzenberg, J.; Zhang, Y.; Hu, M. Mixing state of elemental carbon and non-light-absorbing aerosol components derived from in situ particle optical properties at Xinken in Pearl River Delta of China. *J. Geophys. Res.* **2006**, *11*. [[CrossRef](#)]
6. Pope, C.A.; Dockery, D.W. Health effects of fine particulate air pollution: Lines that connect. *J. Air Waste Manag. Assoc.* **2006**, *56*, 709–742. [[CrossRef](#)] [[PubMed](#)]
7. Chen, P.; Bi, X.; Zhang, J.; Wu, J.; Feng, Y. Assessment of heavy metal pollution characteristics and human health risk of exposure to ambient PM<sub>2.5</sub> in Tianjin, China. *Particuology* **2015**, *20*, 1041–1109. [[CrossRef](#)]
8. Block, M.L.; Elder, A.; Auten, R.L.; Bilbo, S.D.; Chen, H.; Chen, J.C.; Cory-Slechta, D.A.; Costa, D.; Diaz-Sanchez, D.; Dorman, D.C.; et al. The outdoor air pollution and brain health workshop. *Neurotoxicology* **2012**, *33*, 972–984. [[CrossRef](#)] [[PubMed](#)]
9. Cacciottolo, M.; Wang, X.; Driscoll, I.; Woodward, N.; Saffari, A.; Reyes, J.; Serre, M.L.; Vizuete, W.; Sioutas, C.; Morgan, T.E.; et al. Particulate air pollutants, APOE alleles and their contributions to cognitive impairment in older women and to amyloidogenesis in experimental models. *Transl. Psychiatry* **2017**, *7*. [[CrossRef](#)] [[PubMed](#)]
10. Zhang, N.; Han, B.; He, F.; Xu, J.; Niu, C.; Zhou, J.; Kong, S.; Bai, Z.; Xu, H. Characterization, health risk of heavy metals, and source apportionment of atmospheric PM<sub>2.5</sub> to children in summer and winter: An exposure panel study in Tianjin, China. *Air Qual. Atmos. Health* **2015**, *8*, 347–357. [[CrossRef](#)]
11. Lai, C.H.; Lin, C.H.; Liao, C.C. Respiratory deposition and health risk of inhalation of particle-bound heavy metals in the carbon black feeding area of a tire manufacturer. *Air. Qual. Atmos. Health* **2017**. [[CrossRef](#)]
12. Heys, K.A.; Shore, R.F.; Pereira, M.G.; Jones, K.C.; Martin, F.L. Risk assessment of environmental mixture effects. *RSC Adv.* **2016**, *6*, 47844–47857. [[CrossRef](#)]
13. Rodriguez-Espinosa, P.F.; Flores-Rangel, R.M.; Mugica-Alvarez, V.; Morales-Garcia, S.S. Sources of trace metals in PM<sub>10</sub> from a petrochemical industrial complex in Northern Mexico. *Air Qual. Atmos. Health* **2017**, *10*, 69–84. [[CrossRef](#)]
14. Järup, L. Hazards of heavy metal contamination. *Br. Med. Bull.* **2003**, *68*, 167–182. [[CrossRef](#)] [[PubMed](#)]
15. Hellström, L.; Elinder, C.-G.; Dahlberg, B.; Lundberg, M.; Järup, L.; Persson, B.; Axelson, O. Cadmium exposure and end-stage renal disease. *Am. J. Kidney Dis.* **2001**, *38*, 10011–11008. [[CrossRef](#)] [[PubMed](#)]
16. Bellinger, D.C. Teratogen update: Lead and pregnancy. *Birth Defect. Res. Part A Clin. Mol. Teratol.* **2005**, *73*, 409–420. [[CrossRef](#)] [[PubMed](#)]
17. Shao, L.; Shi, Z.; Jones, T.P.; Li, J.; Whittaker, A.G.; Bérubé, K.A. Bioreactivity of particulate matter in Beijing air: Results from plasmid DNA assay. *Sci. Total Environ.* **2006**, *367*, 261–272. [[CrossRef](#)] [[PubMed](#)]
18. Liu, K.; Shang, Q.; Wan, C.; Song, P.; Ma, C.; Cao, L. Characteristics and sources of heavy metals in PM<sub>2.5</sub> during a typical haze episode in rural and urban areas in Taiyuan, China. *Atmosphere* **2018**, *9*, 2. [[CrossRef](#)]

19. Hu, X.; Zhang, Y.; Ding, Z.; Wang, T.; Lian, H.; Sun, Y.; Wu, J. Bioaccessibility and health risk of arsenic and heavy metals (Cd, Co, Cr, Cu, Ni, Pb, Zn and Mn) in TSP and PM<sub>2.5</sub> in Nanjing, China. *Atmos. Environ.* **2012**, *57*, 146–152. [[CrossRef](#)]
20. USEPA. Risk Assessment Guidance for Superfund (RAGS). Part A (1989): Human Health Evaluation Manual; Part E (2005): Supplemental Guidance for Dermal Risk Assessment; Part F (2009): Supplemental Guidance for Inhalation Risk Assessment. Available online: <https://www.epa.gov/risk/risk-assessment-guidance-superfund-rags-part> (accessed on 24 January 2018).
21. USEPA. Risk Characterization Handbook. 2000. Available online: <https://www.epa.gov/risk/risk-characterization-handbook> (accessed on 24 January 2018).
22. Wang, Z.; Liu, S.; Chen, X.; Lin, C. Estimates of the exposed dermal surface area of Chinese in view of human health risk assessment. *J. Saf. Environ.* **2008**, *8*, 1521–1556. (In Chinese)
23. Ferreira-Baptista, L.; De Miguel, E. Geochemistry and risk assessment of street dust in Luanda, Angola: A tropical urban environment. *Atmos. Environ.* **2005**, *38*, 4501–4512. [[CrossRef](#)]
24. Peng, X.; Shi, G.L.; Liu, G.R.; Xu, J.; Tian, Y.Z.; Zhang, Y.F.; Feng, Y.C.; Russell, A.G. Source apportionment and heavy metal health risk (HMHR) quantification from sources in a southern city in China, using an ME2-HMHR model. *Environ. Pollut.* **2017**, *221*, 3335–3342. [[CrossRef](#)] [[PubMed](#)]
25. Querol, X.; Pey, J.; Minguillón, M.; Pérez, N.; Alastuey, A.; Viana, M. PM speciation and sources in Mexico during the MILAGRO-2006 Campaign. *Atmos. Chem. Phys.* **2008**, *8*, 111–128. [[CrossRef](#)]
26. USEPA. Regional Screening Levels (RSLs)—Generic Tables (November 2017). Available online: <https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables-november-2017> (accessed on 24 January 2018).
27. Gao, J.; Wang, K.; Wang, Y.; Liu, S.; Zhu, C.; Hao, J.; Liu, H.; Hua, S.; Tian, H. Temporal-spatial characteristics and source apportionment of PM<sub>2.5</sub> as well as its associated chemical species in the Beijing-Tianjin-Hebei region of China. *Environ. Pollut.* **2017**, *233*, 714–724. [[CrossRef](#)] [[PubMed](#)]
28. Wang, J.; Hu, Z.; Chen, Y.; Chen, Z.; Xu, S. Contamination characteristics and possible sources of PM<sub>10</sub> and PM<sub>2.5</sub> in different functional areas of Shanghai, China. *Atmos. Environ.* **2013**, *68*, 221–229. [[CrossRef](#)]
29. Fang, G.; Chang, C.; Chu, C.; Wu, Y.; Fu, P.; Yang, I.; Chen, M. Characterization of particulate, metallic elements of TSP, PM<sub>2.5</sub> and PM<sub>2.5-10</sub> aerosols at a farm sampling site in Taiwan, Taichung. *Sci. Total Environ.* **2003**, *308*, 157–166. [[CrossRef](#)]
30. Wang, X.; Bi, X.; Sheng, G.; Fu, J.M. Chemical composition and sources of PM<sub>10</sub> and PM<sub>2.5</sub> aerosols in Guangzhou, China. *Environ. Monit. Assess.* **2006**, *119*, 425–439. [[CrossRef](#)] [[PubMed](#)]
31. Tan, J.; Duan, J.; Ma, Y.; Yang, F.M.; Cheng, Y.; He, K.B.; Yu, Y.C.; Wang, J.W. Source of atmospheric heavy metals in winter in Foshan, China. *Sci. Total Environ.* **2014**, *493*, 262–270. [[CrossRef](#)] [[PubMed](#)]
32. Lee, B.K.; Hieu, N.T. Seasonal variation and sources of heavy metals in atmospheric aerosols in a residential area of Ulsan, Korea. *Aerosol Air Qual. Res.* **2011**, *11*, 679–688. [[CrossRef](#)]
33. Chang, S.H.; Wang, K.S.; Chang, H.F.; Ni, W.W.; Wu, B.J.; Wong, R.H.; Lee, H.S. Comparison of source identification of metals in road-dust and soil. *Soil Sediment Contam.* **2009**, *18*, 669–683. [[CrossRef](#)]
34. Lee, B.K.; Jun, N.Y.; Lee, H.K. Comparison of particular matter characteristics before, during and after asian dust events in incheon and Ulsan, Korea. *Atmos. Environ.* **2004**, *38*, 1535–1545. [[CrossRef](#)]
35. Zhao, J.; Zhang, F.; Xu, Y.; Chen, J.; Yin, L.; Shang, X.; Xu, L. Chemical characteristics of particulate matter during a heavy dust episode in a coastal city, Xiamen, 2010. *Aerosol Air Qual. Res.* **2011**, *11*, 299–308. [[CrossRef](#)]
36. Lim, J.M.; Lee, J.H.; Moon, J.H.; Chung, Y.S.; Kim, K.H. Airborne PM<sub>10</sub> and metals from multifarious sources in an industrial complex area. *Atmos. Res.* **2010**, *96*, 53–64. [[CrossRef](#)]
37. Taner, S.; Pekey, B.; Pekey, H. Fine particulate matter in the indoor air of barbeque restaurants: Elemental compositions, sources and health risks. *Sci. Total Environ.* **2013**, *454–455*, 79–87. [[CrossRef](#)] [[PubMed](#)]
38. Manoli, E.; Voutsas, D.; Samara, C. Chemical Characterization and source identification/apportionment of fine and coarse air particles in Thessaloniki, Greece. *Atmos. Environ.* **2002**, *36*, 949–961. [[CrossRef](#)]
39. Cheng, X.; Huang, Y.; Long, Z.; Ni, S.; Shi, Z.; Zhang, C. Characteristics, sources and health risk assessment of trace metals in PM<sub>10</sub> in Panzhuhua, China. *Bull. Environ. Contam. Toxicol.* **2016**, *98*, 76–83. [[CrossRef](#)] [[PubMed](#)]

40. Castillo, S.; de la Rosa, J.D.; Sánchez de la Campa, A.M.; González-Castanedo, Y.; Fernández-Caliani, J.C.; Gonzalez, I.; Romero, A. Contribution of mine wastes to atmospheric metal deposition in the surrounding area of an abandoned heavily polluted mining district (Rio Tinto Mines, Spain). *Sci. Total Environ.* **2013**, *449*, 363–372. [[CrossRef](#)] [[PubMed](#)]
41. Allen, A.G.; Nemitz, E.; Shi, J.P.; Harrison, R.M.; Greenwood, J.C. Size distribution of trace metals in atmospheric aerosol in the United Kingdom. *Atmos. Environ.* **2001**, *35*, 4581–4591. [[CrossRef](#)]
42. Mansha, M.; Ghauri, B.; Rahman, S.; Amman, A. Characterization and source apportionment of ambient air particulate matter (PM<sub>2.5</sub>) in Karachi. *Sci. Total Environ.* **2012**, *425*, 176–183. [[CrossRef](#)] [[PubMed](#)]
43. Viana, M.; Kuhlbusch, T.A.J.; Querol, X.; Alastuey, A.; Harrison, R.M.; Hopke, P.K.; Winiwarter, W.; Vallius, M.; Szidat, S.; Prévôt, A.S.H. Source apportionment of particulate matter in Europe: A review of methods and results. *J. Aerosol Sci.* **2008**, *39*, 827–849. [[CrossRef](#)]
44. Samara, C.; Voutsas, D. Size distribution of airborne particulate matter and associated heavy metals in the roadside environment. *Chemosphere* **2005**, *59*, 1197–1206. [[CrossRef](#)] [[PubMed](#)]
45. Liacos, J.W.; Kam, W.; Delfino, R.J.; Schauer, J.J.; Sioutas, C. Characterization of organic, metal and trace element PM<sub>2.5</sub> species and derivation of freeway-based emission rates in Los Angeles, CA. *Sci. Total Environ.* **2012**, *435–436*, 159–166. [[CrossRef](#)] [[PubMed](#)]



© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).