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Source Apportionment of Topsoil Heavy Metals and Associated Health and Ecological Risk Assessments in a Typical Hazy City of the North China Plain

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Abstract: The North China Plain (NCP) is the most populous plain in China and forms the core of the Beijing-Tianjin-Hebei economic circle. With urbanization, anthropogenic heavy metals have increasingly dispersed and accumulated in urban topsoil, especially in hazy cities. To investigate the major sources of haze and their relation to topsoil heavy metals concentrations in cities of the NCP, 220 topsoil samples (0–10 cm) were collected from Shijiazhuang city (capital of Hebei Province). The concentrations of eight selected metals were determined. Statistical and spatial distribution analyses suggest that coal combustion and industrial processes (Ni, Cr, Cd and Hg) were the dominant anthropogenic sources of haze in Shijiazhuang city, followed by vehicle exhausts (Pb, Zn Cu and Hg). Contrastingly, As was derived from parent materials of the NCP. A health risk assessment showed that Pb, Cr and As pose significant non-carcinogenic risks to children (hazard index > 1) via oral ingestion. A potential carcinogenic risk to children (CRs > 10^{-4}) is also posed by As. While Cd and Hg do not pose health risks in Shijiazhuang city, they may pose important ecological risks as ecological risk factors > 40 were observed, resulting in ecological risk indexes of 150–600 (moderate to considerable ecological risks).

Keywords: hazy city; sources apportionment; topsoil heavy metal; health and ecological risks; North China Plain

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1. Introduction

The North China Plain (NCP) is a typical Cenozoic sedimentary basin and one of the largest alluvial plains in eastern Asia. Two municipalities (Beijing and Tianjin) and five provinces (Hebei, Shandong, Henan, Anhui, and Jiangsu) are located within the NCP, which has a total area of 300,000 km^2 and is located between 36°00′–40°00′ N and 114°00′–118°00′ E [1]. The NCP is the most populous plain in China with a population of 339 million, accounting for 24.2% of China's total population in 2019. Due to rapid urbanization and industrialization, large cities in the NCP, such as Beijing, Tianjin, Shijiazhuang, Zhengzhou, Qingdao and Xuzhou are facing severe environmental problems due to soil pollution by heavy metals, which are persistent and toxic [2–5]. Heavy metal pollution in urban soils influences the ecological functionality of cities and poses strong risks to human health [6–9].

The sources of heavy metals in urban soils are widespread and complex [9,10]. Soil is a natural buffer that controls the transport of heavy metals to the atmosphere, hydrosphere and biosphere [11]. In addition, soil acts as a geochemical sink; once contaminated, heavy metals adsorbed on the fine particles of urban topsoil can be easily transferred into the human body via hand-to-mouth and dermal contact pathways [4,12]. In particular, in the case of outdoor activities for children, the process of resuspension by wind erosion or the action of feet usually occurs [12]. In fact, heavy metals that are toxic, non-biodegradable and accumulative often accumulate in the top layer of urban soil [13]. This can alter the balance of biogeochemical cycles in food webs and deteriorate soil biology and functionality, causing serious environmental and ecological problems [9,10,14,15]. In terms of biological function, Cu, Zn, Ni and Cr are essential trace elements. Low concentrations of these elements are required for the growth and development of soil, plants and humans, however, excessive contents and long-term exposure can cause the bioaccumulation of toxins, with irritant and necrotic effects [16]. Cd and Pb are thought to be non-essential; however, they can pose risks if their bioavailability in soil is high. The least soluble heavy metal in soil is Pb, which is considered to be a potential human carcinogen and a highly toxic metal and neurotoxin [13]. High Cd concentrations in soil can interfere with the transport, absorption and activities of plant Ca, K, Mg and P [17], and have carcinogenic, mutagenic, genotoxic and immunotoxic effects. In addition, As and Hg are toxic and carcinogenic to humans even at low levels [4]. These heavy metals can be readily transferred to the body by ingestion, inhalation or dermal absorption, where they influence the nervous system, endocrine system, immune system, hematopoietic function and normal cellular metabolism [18].

Many studies on the distribution and sources of topsoil heavy metals have been conducted in large cities in the NCP (e.g., Beijing, Tianjin, Zhengzhou, Qingdao, Xuzhou). Liang (2010) [19] found that commercial activities and traffic make large contributions to soil heavy metal accumulation in Zhengzhou, which could be because this city has a short history of urbanization and lacks high industrial activities. Cu is the main heavy metal pollutant in Zhengzhou's urban soil [20], while there is no As pollution despite As contents being significantly higher in urban soil than in suburban soil [21]. Wang and Qin (2006) [22] showed that the enrichment of Zn, Cd, As and Hg were high, while those of Cu, Ni and Cr were low in the urban topsoil of Xuzhou. The spatial distributions of Zn, Cu, Pb and Cd pollution are mainly related to transportation and other sources of pollution diffusion; however, high concentrations of As and Hg are mainly concentrated in industrial areas [22]. Similarly, in the urban soils around the Tanggu chemical industrial district (Tianjin), there is Cu, Pb and Zn pollution that has mainly originated from vehicular transport and industrial discharge, As and Hg pollution attributed to coal combustion and emissions from the chemical industry, and Cr and Ni pollution derived from the soil parent material [18]. In the topsoil of the urban renewal area in Beijing, the concentrations of Cu, Pb, Cd, Zn, and especially Hg, are high and strongly influenced by anthropogenic or chemical industry activities, while there is Ni, As, V and Cr that has mainly originated from the natural parent materials of soils in the NCP [23]. In addition, high heavy metal concentrations are mainly found in the soils of industrial cities and rapidly developing cities, such as Qingdao [4]. However, the sources of As, Cr and Ni are highly variable among cities in the NCP.

Shijiazhuang is one of the most important cities in the Beijing-Tianjin-Hebei Economic Circle (Figure 1A,B). Over the past five decades, Shijiazhuang has developed from a rural area to a metropolitan city with a population of up to 12 million [24], and is facing severe pressures from urbanization and industrialization [25–27]. In fact, Shijiazhuang is informally called the "Hazy City" due to its air pollution. However, few have paid attention to the major cause (source) of haze from the perspective of topsoil heavy metals. In addition, the potential risks to human health and ecology posed by topsoil heavy metals in hazy cities in the NCP must also be considered [3,4].

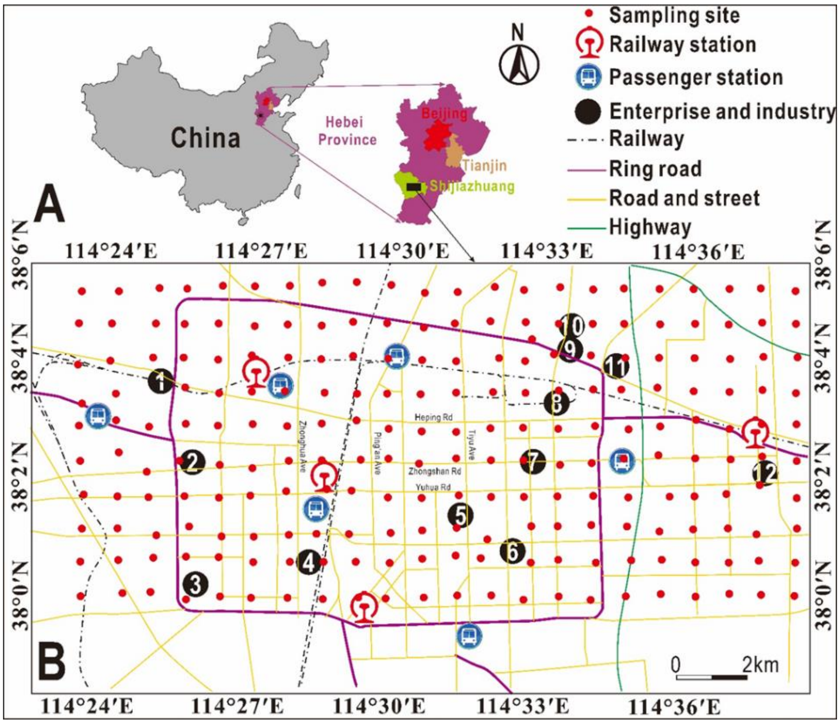

Figure 1. (**A**) The location of Shijiazhuang city in China; (**B**) Distribution of topsoil samples in Shijiazhuang city. Enterprise and industry: 1. Shijiazhuang Huancheng chemical plant, 2. The 54th Research Institute of China Electronics Technology Group Corporation, 3. Shijiazhuang 1st wool textile factory, 4. Shijiazhuang Thermal power plant, 5. Hebei meteorological bureau, 6. Hebei GEO University, 7. Hebei Provincial Imagery and Mapping Agency, 8. Shijiazhuang coking plant, 9. Shijiazhuang Shuguang chemical fertilizer plant, 10. Shijiazhuang Shuguang pharmaceutical factory, 11. Shijiazhuang Magang manufacturing district, 12. Shijiazhuang Weisheng pharmaceutical corporation.

In this study, we determined concentrations of eight heavy metals (Cu, Pb, Zn, Cr As, Cd, Ni, and Hg) in topsoil sampled from Shijiazhuang. The specific objectives were to: (1) assess the enrichment level of heavy metals in the topsoil; (2) determine the dominant causes of haze in relation to topsoil heavy metals; and (3) evaluate the health and ecological risks posed by topsoil heavy metals to inform better management practices.

2. Materials and Methods

2.1. Study Area

The NCP is characterized by flat terrain and numerous rivers and lakes. It has a convenient transportation system and a developed economy, and has developed into the political, economic and cultural centre of China. Shijiazhuang, the capital city of Hebei Province, is located in the hinterland of the NCP, bordering Beijing and Tianjin to the north, the Bohai Sea to the east and the Taihang Mountains to the west [28]. Geographically, Shijiazhuang is in the south-central part of Hebei Province within the NCP. It is mostly covered by cinnamon soils [29] and, from west to east, consists of piedmont alluvial, central alluvial-lacustrine, and littoral alluvial plains [12]. Shijiazhuang is also a large industrial city famous for raw material and energy production and its steel, power and cement industries [30]. In addition, Shijiazhuang is one of China's important commodity distribution centres, is a large northern commercial city, and is one of the main hosts of national trade conventions and exhibitions. It is also one of China's main railway transportation hubs, where four railways lines meet. In 2016, the number of vehicles was more than 2.0 million [30]. Shijiazhuang has obvious geographical advantages in terms of politics, economy and culture. The core urban area of Shijiazhuang is mainly a rectangular area (within one ring) bounded by Pingan Ave, Zhongshan Rd, Zhonghua Ave, Heping Rd, Tiyu Ave and Yuhua Rd, and includes eight main roads; three horizontal and five vertical [31]. The region has high concentrations of workplaces, as well as social, economic, financial and trade activities. It is a typical centre of business and trade, economy and finance, culture and entertainment, and social and political activities. Shijiazhuang is characterized by a semi-arid continental monsoon climate with an annual mean temperature of 12–13 °C, annual precipitation of 400–800 mm and mean potential evaporation rate of 1100–1800 mm/year [24]. The average annual air humidity is 65% and about 63–70% of the annual precipitation fells from June to September.

2.2. Sample Collection and Chemical Analysis

The sampling methods in this study comply with the Geological Survey Technology Standard of the China Geological Survey. A total of 220 topsoil (0–10 cm) samples were collected from the central urban area of Shijiazhuang city and its surrounding suburban area according to the sampling density of 1 km^2 per sample (Figure 1). During the sampling, we tried to avoid the interference of external soil and then removed impurities and gravel from the soil surface. Soil samples of about 1 kg were collected in a clean cloth bag with labels, and then dried naturally. The topsoil samples were gently tapped with a mallet before being sifted so that the soil samples remain in their natural size state. The sample was bottled with a nylon sieve with a grain size of 500 g less than 0.8 mm (20 mesh).

The Cr, Ni, Zn, Cu, and Pb concentrations were determined by X-ray fluorescence spectrometry (XRF) with detection limits of 2, 1, 2, 1, 1 mg/kg, respectively. The concentration of Cd in the samples were measured by ICP-MS (detection limits: 0.02 mg/kg) after the digestion (HCl-HNO_3-HF-$HClO_4$). For the extraction of As and Hg metals, the topsoil samples were digested with aqua regia (HNO_3: HCl = 1:3), and atomic fluorescence spectrometry (AFS) was used to determine their concentrations (with detection limits of 0.05 and 0.0003 mg/kg, respectively). The measure accuracy was verified using the Chinese standardized reference material (GSS-1). For quality control, reagent blanks, duplicate samples, reference standard and external monitor samples were inserted among the soil samples to evaluate the analysis methods. The recoveries were accepted within the range from 81.0 to 119%.

2.3. Assessment Method

2.3.1. Method for Contamination Assessment

Contamination factor (CF) has been used to assess the pollution of heavy metals in topsoil. It was determined by the ratio of the concentration of heavy metal n for the sampled soil (C_n) to the values for the background (B_n). The background values of the NCP (average regional values) were adopted to calculate the CF values for the selected metals [32]. The value of CF was interpreted using four classes: low pollution (CF < 1), moderate pollution (1 ≤ CF < 3), high pollution (3 ≤ CF < 6) and very high pollution (CF ≥ 6) [7,33].

The pollution load index (PLI) has been used to assess soil pollution from heavy metals. It is calculated by the following equation:

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times \ldots \times CF_n} \quad (1)$$

where n represents the number of metals. The PLI was interpreted unpolluted (0–1), unpolluted to moderately polluted (1–2), moderately polluted (2–3), moderately to highly polluted (3–4), highly polluted (4–5) and very polluted soil (>5) [8].

2.3.2. Method for Human Health Risk Assessment

Human health risk assessment is the process of estimating the probability of adverse health effects of hazard chemicals to human health according to human exposure characters (see details in Supplementary Materials). Hazard quotient (HQ) is typically used to evaluate the non–carcinogenic risk level of human exposure for one metal [4]. While, for multiple chemicals, the sum of the HQ values of all chemicals is expressed as a hazard index (HI) to assess the overall non–carcinogenic risk effects. Whereas for carcinogens the dose is multiplied by the corresponding slope factor (SF) to calculate carcinogenic risks (CR), to indicate the incremental probability of an individual developing cancer over a lifetime as a result of exposure to the potential carcinogen [3]. Generally, the values of HI > 1 and CR > 10^{-4}, respectively, represent adverse effects to human health and lifetime carcinogenic risks [4]. The reference values and data source of the abbreviation for the parameters were shown in Tables S1 and S2.

2.3.3. Method for Ecological Risk Assessment

When considering the different toxicities of the heavy metals to human and biota, the potential ecological risk index (RI) was developed by Hakanson (1980) to assess the pollution degree and ecological risk from heavy metals in soil [31]. It takes in to account the CF, potential ecological risk factor (E_r) and the toxicological response factor (T_r) (i.e., Hg = 40, Cd = 30, As = 10, Pb = Cu = Ni = 5; Cr = 2; Zn = 1) of each heavy metal (i) [6,34] and is calculated by the following equation:

$$RI = \sum_{1}^{n} E_r^i = \sum_{1}^{n} E_r^i \times CF^i \tag{2}$$

The ecological risk levels can indicate low risk (E_r^i< 40, RI < 150), moderate risk ($40 \leq E_r^i < 80$, $150 \leq RI < 300$), considerable risk ($80 \leq E_r^i < 160$, $300 \leq RI < 600$), very high risk ($160 \leq E_r^i < 320$, $600 \leq RI$), and dangerous ($E_r^i > 320$) [23,33].

2.4. Data Analysis

Descriptive statistics and data analyses were conducted with Microsoft Excel 2019 and IBM SPSS Statistics Version 21. Pearson's correlation coefficient analysis and principal component analysis were used to determine the possible sources of eight heavy metals in the urban topsoils. Mapping that shows spatial distributions of heavy metals was visualized using ArcGIS version 9.0 (ESRI, Redlands, CA, USA).

3. Results and Discussion

3.1. Heavy Metal Accumulation in Topsoil

Table 1 shows the statistical characteristics of the eight heavy metals and Al_2O_3 (*n* = 220) in Shijiazhuang city. The K-S test results show that none of the eight metals had normally distributed concentration data (significance > 0.1). The average concentrations of metals of topsoil (in mg/kg) were compared and can be ranked as follows: Zn (105) > Cr (71.9) > Pb (31), Ni (28.2) and Cu (27.4) > As (9.42) > Cd (0.27) > Hg (0.113) (Table 1). This ranking is similar to those of other urban topsoils around the world [5]. The coefficient of variation (CV) of the metals in Shijiazhuang city decreased in the order Cd > Hg > 100% > Zn > Cr > Pb > As > Ni > Cu > Al_2O_3, indicating high variations of Cd, Hg and Zn. The contamination factors (CFs) of the eight metals were in descending order of Hg > Cd > Zn > Pb > Cu > Cr > 1 > Ni > As (Table 1). Of the sampling sites, 85.0%, 93.2%, 87.3%, 83.6% and 70.9% were moderately contaminated by Cd, Zn, Pb, Cu and Cr, respectively, while 18.2%, 53.2% and 28.2% were moderately, highly and very highly contaminated by Hg, respectively. In addition, 97.7% of sites showed pollution load indexes (PLIs) greater than 1. The average contamination level was 1.67 (unpolluted to moderately polluted) with only 18.2% of observations being greater than the moderate pollution level (PLI > 2). Some 79.5% of sites were unpolluted to moderately polluted and only 2.3% were unpolluted. These results suggest that the metals in the topsoil of Shijiazhuang city differed greatly with respect to pollution source and concentration, especially for Hg, Zn, Pb, Cu, Cd and Cr.

The economic development level and industrial structure vary among cities throughout China; therefore, the impacts of human activities on topsoil are diverse [4]. In general, the concentrations of heavy metals in the topsoil of different types of cities usually follow the order: industry-based cities (such as Baoji, Qingdao and Dongguan) > more developed cities (Hangzhou and Lishui) > metropoles (such as Beijing, Tianjin, Shanghai and Guangzhou) > western underdeveloped cities (Urumqi, Xining and Lhasa) ≈ county and agricultural areas (such as Xiangfen, Wulian and Xinglonggang) as shown in Table 2. The concentrations of most heavy metals (except As and Hg, but especially Zn and Cr) were higher in Shijiazhuang city than in county and agricultural areas and underdeveloped cities, and were generally lower than in some metropoles such as Shanghai and Tianjin. In such urbanization -leading metropoles, the potential emission intensity of anthropogenic heavy metal pollutants, including Pb, Cu and Zn in Shijiazhuang city were much weaker than those in industry-based and more developed cities with a large population.

Table 1. Statistical characteristic values of heavy metal concentrations (mg/kg) in Shijiazhuang city.

	Cr	Ni	Cd	Pb	Cu	Zn	As	Hg	Al_2O_3
Min.	54.9	20.2	0.13	16.7	18.7	54.0	5.2	0.019	10.59
Max.	457.7	99.0	5.22	85.1	55.4	813.9	23.3	1.598	14.31
Median	68.9	27.4	0.200	27.6	26.7	88.5	9.1	0.092	12.7
Average	71.8	28.2	0.27	31.0	27.4	104.5	9.4	0.113	12.66
CV%	38.9	20.2	135.06	35.4	19.5	66.8	23.5	106.661	4.43
SD	28.0	5.7	0.37	11.0	5.3	69.8	2.2	0.120	0.56
CF	1.09	0.88	2.43	1.41	1.19	1.69	0.86	5.64	0.99
North China Plain background [32]	66	32	0.113	22	23	62	11	0.020	12.84
Proportion above the background	69.5%	7.3%	100.0%	87.7%	82.7%	98.2%	8.2%	99.5%	39.1%

3.2. Spatial Distribution of Heavy Metals

Spatially, the areas defined by Zhonghua Ave, Heping Rd, Tiyu Ave and Yuhua Rd (Figure 1B) represent the core areas of Shijiazhuang city with the highest traffic flows, greatest workplace densities and highly concentrated social and economic activities. These areas usually showed the highest concentrations of Cu, Pb and Zn. The topsoil adjacent to railway stations and bus stations in northern Shijiazhuang also showed high concentrations of Cu, Pb and Zn (Figures 1B and 2). In addition, the areas with high values corresponded to the industrial areas in the middle, east and northeast of Shijiazhuang (Figure 1B). In contrast, high concentrations of Cr, Cd and Ni were distributed in the industrial area in the northeast of the urban area, which includes steel, coking, cement and coal machinery plants. Areas of high As concentrations occurred near the pharmaceutical plants in the north-central part of Shijiazhuang city, while, other areas had As concentrations below the background value. In contrast, there was a wide distribution of high-Hg-concentration areas suggesting that Hg pollution in the Shijiazhuang urban area is widespread and has multiple sources.

3.3. Source Identification

Correlation analysis (CA) and principal component analysis (PCA) were used to identify the sources of heavy metals in urban topsoil in Shijiazhuang city (Tables S3 and S4, respectively). A total of four principal components (PC; eigenvalues > 1) were extracted (Figure 3).

For F1, significant positive loading values (>0.9) of Cr, Ni and Cd usually reflect contamination by atmospheric deposits in urban soils [35]. Coal-burning power plants and smelters could cause high Cr and Ni accumulation in nearby topsoil [5,36]. Previous studies show that high concentrations of Cr, Ni and Cu are discharged during metal electroplating and rolling processes, and have accumulated as dust in streets near the urban industrial area of Delhi city, India [37]. Yuswir et al. (2015) showed that Cd and Cr in urban topsoil may have originated from the electronics and semiconductor industries in Klang district, Malaysia [38]. Therefore, we infer that PC1 is primarily controlled by industrial activities and coal burning.

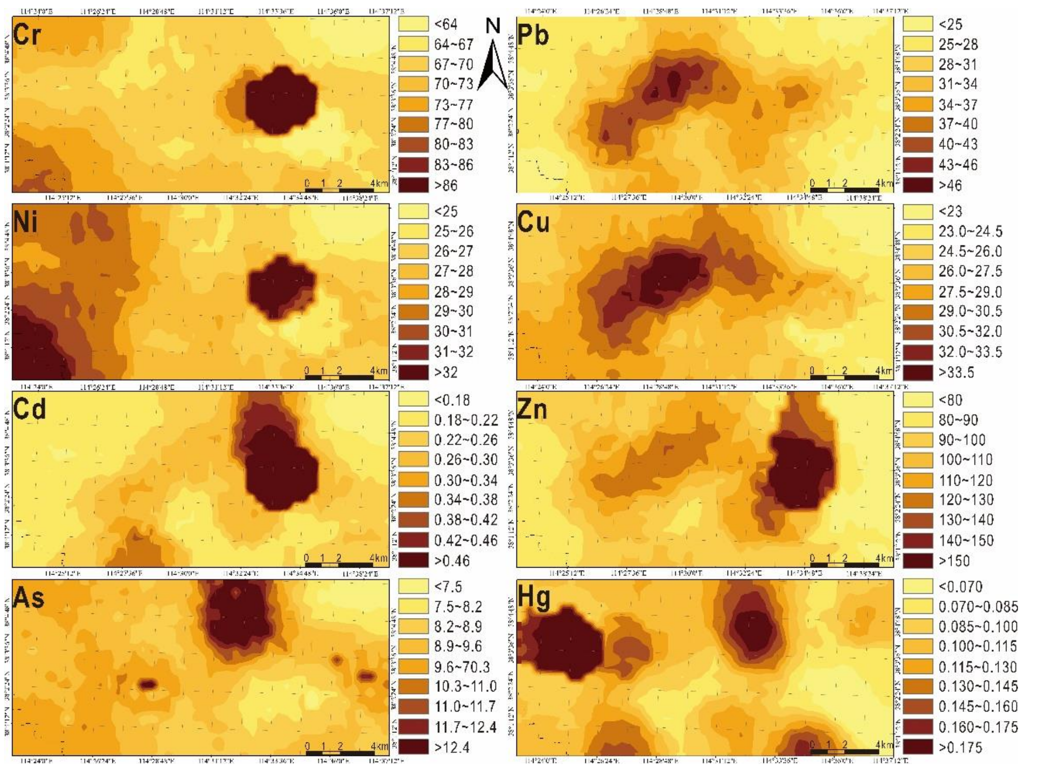

Figure 2. Spatial variations of eight heavy metals in Shijiazhuang city.

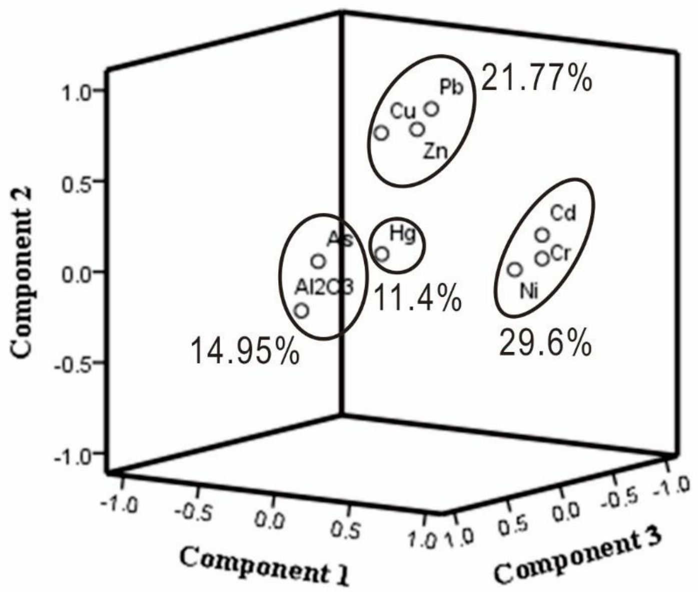

Figure 3. 3D plot of factor loadings of studied metals and Al_2O_3 of topsoil in Shijiazhuang.

Principal component F2 also had high loadings on Pb, Cu and Zn (0.7−0.9). Several studies have proven that vehicle emissions are the main source of Pb in urban topsoil [39–41]. Zn and Cu may come from mechanical wear, brake pads, oil leak pools and cylinder head washers on vehicles [42,43]. Engine and tire oil production requires Zn as an additive [17]. Cu, Pb and Zn pollution in urban topsoil where industrial factories and plants once operated remains an unresolved problem, especially in large cities of China [18,44]. Thus, F2 represents traffic sources coupled with industrial input.

For PC F3, only Al_2O_3 and As were grouped in a positive correlation (r = 0.254, $p < 0.01$) (Tables S3 and S4). There were low concentrations of Al_2O_3 and As (comparable to background levels) and low CF (<1) and CV% values (4.43% and 23.5%, respectively). Similar results have been reported in the eastern Hebei plain (Hebei Province) [45]. Therefore, F3 primarily indicates natural sources of heavy metal input.

Table 2. Comparison of heavy metal concentrations (mean) observed in this study with those found in other types of cities in China (mg/kg).

Concentration	Pb	Cd	Cr	Cu	Zn	Ni	As	Hg	Reference
Industrial based cities									
Shenyang	11,700	1.1	67.9	92.45	235	–	22.7	0.39	[4]
Anshan	45.1	0.86	69.9	52.3	213	33.5	–	–	[37]
Dongguan	160	0.25	74.9	66.6	150.8	44.5	13.3	0.15	[4]
Qingdao	250	0.29	82.15	62.0	209.07	83.8	–	–	[4]
Baoji	25,400	–	102.4	112	1960	72.1	–	–	[4]
More developed cities									
Hangzhou	84.3	1.2	–	46.1	203	–	–	–	[4]
Lishui	63.1	0.53	34.7	35.8	192	12.7	8.81	–	[4]
Metropoles									
Beijing	33.7	0.17	60.3	31.3	83.8	23.3	8.55	0.32	[23]
Shanghai	70.7	0.52	108	59.3	301	31.14	–	–	[4]
Shenzhen	53.59	0.39	–	28.33	72.68	–	–	–	[4]
Tianjin (Tanggu)	45	0.18	81	33	148	39	11	0.43	[18]
Guangzhou	65.4	0.23	22.4	41.6	277	11.1	–	–	[4]
Shijiazhuang	31	0.27	71.9	27.4	105	28.2	9.42	0.113	This study
Underdeveloped cities									
Lhasa	31	0.12	42	21.6	65	21	20.5	0.092	[44]
Xining	24.1	0.15	74	24.5	64	26.1	11.6	0.077	[44]
Urumqi	18.2	0.14	58	30.1	72	27.5	13.3	0.041	[4]
County and Agricultural area									
Shunyi	20	0.14	–	22	70	–	7.9	0.07	[4]
Xiangfen	23	0.2	71	30	82	32	14	0.13	[46]
Ecological demonstration zone									
Wulian	32	0.13	56	22	73	24	–	–	[46]

Principal component F4 was only loaded by Hg (Table S3). However, a 3D-loading plot shows that F4 was distributed in the space constrained by F1, F2 and F3 (Figure 3). This suggests that Hg has multiple-sources. Some 99.5% of the topsoil samples exceeded the background concentration of 0.02 mg/L. This can explain the relatively high average Hg concentrations in comparison to those of underdeveloped cities and agricultural based counties (Table 2).

Table 3 shows that the topsoil Cr concentration in Shijiazhuang was higher than that of Beijing (natural source) and Zhengzhou (non-industrial source). The Cd concentration in Shijiazhuang was higher than in Beijing (anthropogenic and industrial sources) and Tianjin (industrial source). This indicates that coal combustion and industrial processes are the dominant factors causing haze in Shijiazhuang. In contrast, the topsoil Pb concentration in Shijiazhuang was much lower than that in Zhengzhou, which seems to indicate that although there are much greater traffic volumes in central Shijiazhuang city, the influence of traffic emissions on haze is less than those of coal combustion and industrial processes.

Table 3. Statistical characteristic values of heavy metal concentrations (mg/kg) in Shijiazhuang city.

Concentration	Pb	Cd	Cr	Cu	Zn	Ni	As	Hg	Reference
Beijing	33.7	0.17	60.3	31.3	83.8	23.3	8.55	0.32	[23]
Tianjin (Tanggu)	45	0.18	81	33	148	39	11	0.43	[18]
Qingdao	250.17	0.29	82.15	62.04	209.07	83.76	–	–	[4]
Xuzhou	37	0.58	73	34	169	34	39.88	0.29	[22]
Luoyang	65.92	1.71	71.42	85.4	215.75	-	-	-	[4]
Zhengzhou	51.2		59.8		65.4	34.3			[19]
Shijiazhuang	31	0.27	71.9	27.4	104.5	28.2	9.42	0.113	This study

3.4. Health Risk Assessment

The mean HQ and HI values of each metal were calculated to evaluate their non-carcinogenic risks. As shown in Figure 4, due to their high topsoil concentrations or low RfD values, As, Cr and Pb showed high HQ values (>1), which suggests that they present higher non-carcinogenic risks to humans than Cd, Cu, Zn and Hg (<0.1). Oral ingestion is the main exposure pathway for metals in Shijiazhuang, followed by dermal contact. It is noteworthy that children always had higher HI values for each metal than adults, demonstrating that children are at greater risk of metal exposure from topsoil than adults. For example, the HI values of Cr, Pb and As in topsoil were >1 for children. The HI value of Ni was >0.1, indicating a potential health hazard to children [47]. These results indicate that As, Cr, Pb and Ni in topsoil may pose non-carcinogenic risks to children in Shijiazhuang city, while there were acceptable HI values (<1) for adults.

In this study, three exposure pathways of carcinogenic risk (CR) from As and Cd were considered due to their relatively high concentrations in different types of cities (Table 2). However, only CRs due to inhalation were estimated for Cr and Ni [4]. The results show that oral ingestion was the main exposure pathway of As in both children and adults, because the CRs of ~10^{-4} were much greater than the acceptable limit of 10^{-6} (Figure 5). In addition, for children, Cd had a CR value slightly exceeding 10^{-6}, while As had a CR value close to 10^{-6} for the oral ingestion and dermal contact pathways. In contrast, the inhalation CRs of these four metals were much lower than 10^{-6}, suggesting that the inhalation exposure pathway from topsoils in Shijiazhuang city has an acceptable risk.

Given the relatively high concentration of naturally sourced As in Shijiazhuang (11.0 mg/kg), mitigation measures should be taken during earth-moving projects to minimize the exposure of people, especially children. Children near transportation hubs and industrial areas should be protected against the non-carcinogenic risks of Cr, Pb and Ni and the carcinogenic risks of Cd through oral ingestion. It is worth paying additional attention to reducing the emissions of industries and enterprises near urban residential areas.

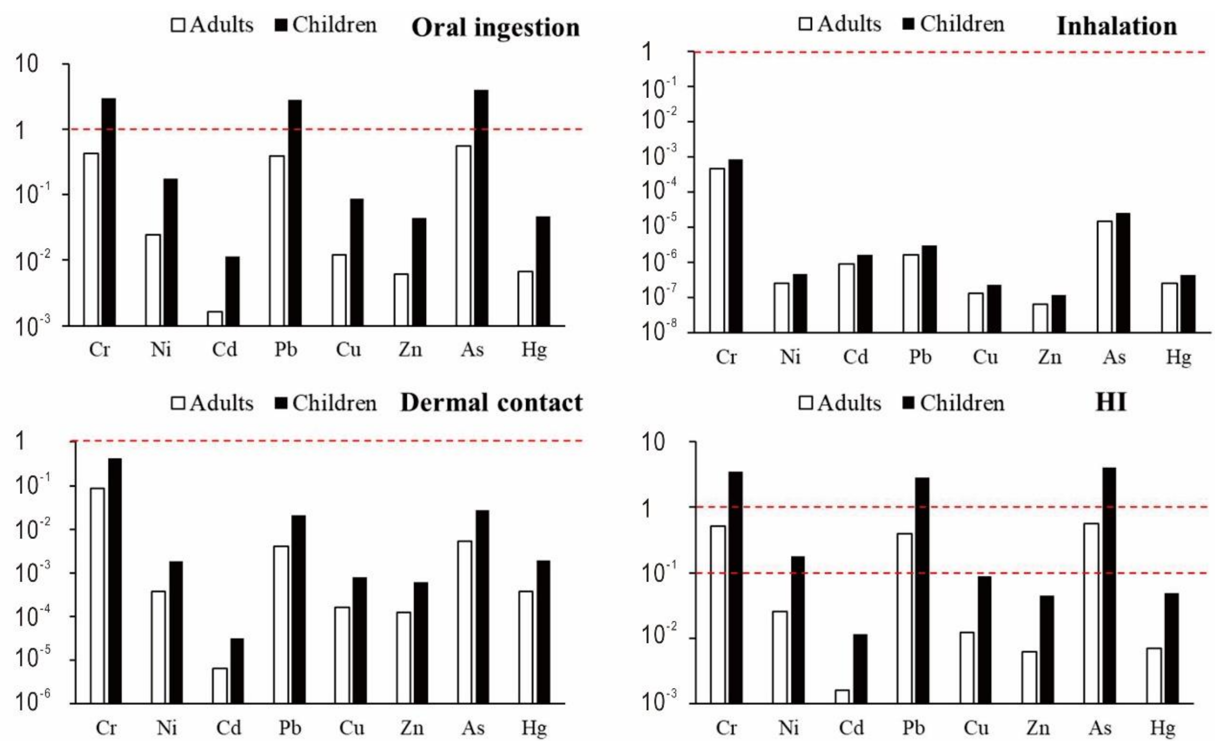

Figure 4. Comparison of HQ and HI values for adults and children through three pathways.

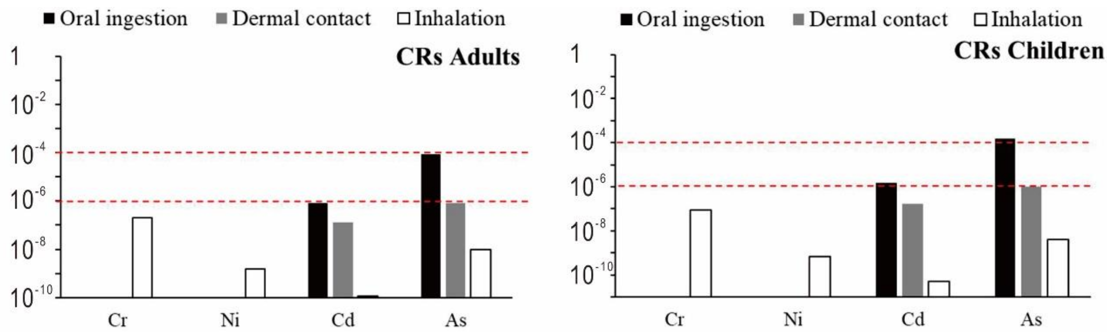

Figure 5. Carcinogenic risk for adults and children through three pathways.

3.5. Potential Ecological Risks

The accumulation of heavy metals in urban topsoil influences urban ecosystems chronically through direct exposure or indirect trophic transfer [34]. Unlike Ni and As, the metals Cr, Cd, Pb, Cu and Zn were enriched in the topsoil of Shijiazhuang city to various degrees (69.5% of the topsoil had concentrations greater than the background). In general, the soil suffered moderate pollution (70.9–93.2% of topsoil with a CF between 1–3 and 79.5% of topsoil with a PLI between 1–2). However, for Cd and Hg in topsoil, 87.7% and 100% of the samples had Er values above 40, while other heavy metals had Er values below 40 (Figure 6). As a result, Shijiazhuang soil is faced with potential ecological risks that are moderate (52.7% of topsoil with RI of 150–300) to considerable (35.5% of topsoil with RI = 300–600).

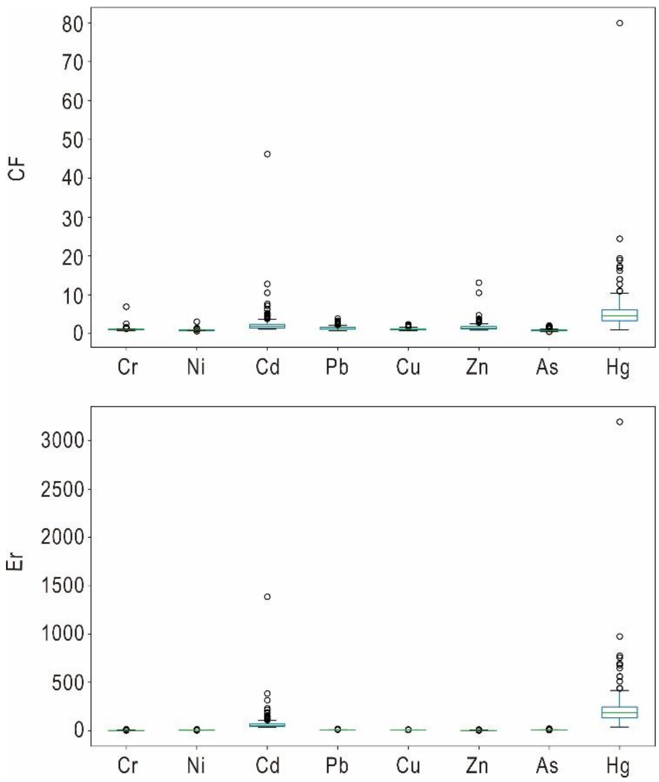

Figure 6. Contamination factor (CF) and potential ecological risk factor (Er) for heavy metals in topsoil from Shijiazhuang city.

Mapping can provide useful information for pollution risk assessment (Figure 7). Heavy metals with a PLI > 1 were observed in 97.7% of topsoil samples, while 94.5% had RI > 150. The highest PLI and RI values were found in the east near the industrial area (with steel, coking, cement and coal machinery plants) in the northeast of the urban area. It is worth noting that the spatial distribution of RI in the topsoil was similar to that of Hg concentrations, while PLI was similar to those of Cr and Cd. Although Cd and Hg do not pose health risks to human, they do pose important ecological risks to the urban area of Shijiazhuang.

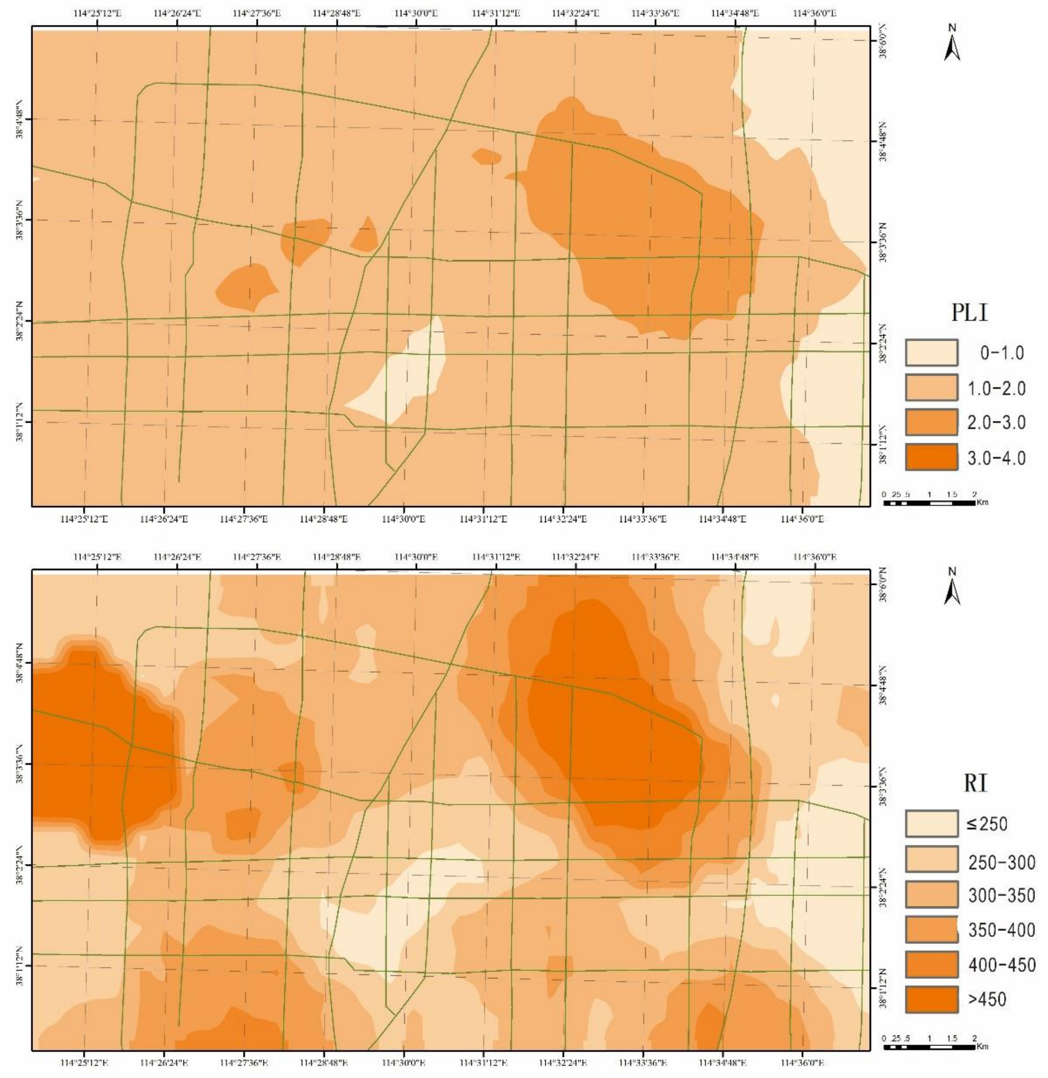

Figure 7. The spatial distribution of the pollution load index (PLI) and potential ecological risk index (RI) of heavy metals from Shijiazhuang city.

4. Conclusions

This study analyzed the sources of heavy metals in topsoil in Shijiazhuang and the associated health and ecological risks. The CA and PCA methods indicated that the major pollution sources were industrial processes, coal-burning emissions and vehicle exhausts. The spatial distributions of traffic and industry have an important influence on the enrichment of anthropogenically sourced heavy metals. High Ni, Cr and Cd levels were concentrated near industrial districts but were also related to coal combustion activities, while high concentrations of Pb, Zn and Cu were mainly attributed to urban transport in central Shijiazhuang city and industrial production around the city. Hg pollution was widespread and showed multiple sources. Coal combustion and industrial production may be the most important factors causing haze in Shijiazhuang.

The health risk assessment indicated that Cr, Cd and Pb concentrations in urban topsoil are generally acceptable, while that of As is not. Arsenic may pose high carcinogenic

($CR > 10^{-4}$) and non-carcinogenic risks (HI > 1) to children through oral ingestion, even though the source of As was mainly parent materials. This shows that contact between local residents and soil As should be avoided during urban development. Therefore, special attention should be paid to As contamination in topsoil and its potential health risks. In addition, Cr and Pb may pose non-carcinogenic risks to children, while Cd may pose carcinogenic risks. Hg can pose significant ecological risks to residents of Shijiazhuang city (35.5% of topsoil had RI = 300–600), even though it is considered to be safe for human health (HI < 1). Studies related to heavy metals in urban topsoil should focus on potential health and ecological risks, rather than simply conducting source analysis or singular risk assessments.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/su131810046/s1, Table S1: Definition and reference value of some parameters for health risk assessment of heavy metal, Table S2: Summary of reference doses (RfD) and slope factors (SF) of heavy metals, Table S3: Rotated component matrix for heavy metals data of urban soils from Shijiazhuang city, Table S4: Correlation matrix for the heavy metals of urban soil in Shijiazhuang city.

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