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Assessment of the Health Effects of Heavy Metals Pollution of Agricultural Soils in the Iron Ore Mining Area of the Northern Piedmont of Mount Wutai, Shanxi Province, China

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Abstract: We have measured the concentrations of toxic elements (Cd, Pb, As, and Hg) in 29 samples from agricultural soils in an iron ore mining area in the northern piedmont of Mount Wutai in Shanxi Province, China. The aim was to evaluate the potential health risks to local inhabitants based on the health risk assessment model derived from the United States Environmental Protection Agency (USEPA). The results show that the concentrations of the four heavy metals exceed their background values, especially in the case of Hg. The pollution level of the four heavy metals can be ordered as follows: Hg > Cd > Pb > As. The spatial distribution of the concentrations of the four heavy metals was uneven: pollution levels were lowest in the basin of the E River, and centered on the E River there was an increasing trend towards the Yukou River in the west and the Yangyan River in the east. In terms of the degree of pollution, this trend can be summarized as: Qingyang River > Yangyan River > Yukou River > E River. The main form of ingestion of the metals was via mouth and nose, and the risk to children is higher than for adults. Iron ore mining was the main cause of the increased concentrations of As and Cd, which represent a cancer risk for humans.

Keywords: northern piedmont area of Mount Wutai; iron mining; agricultural soils; contamination status; health risk assessment

1. Introduction

Heavy metals pollution is a major environmental problem and poses a significant threat to human health [1–3]. Large amounts of various heavy metals are released during mining, smelting, and commercial activities. Heavy metals accumulate in the soil, water, and atmosphere, and thus they constitute a health risk. Their accumulation in agricultural soils clearly presents a major health risk [4,5]. Certain heavy metals are essential for biological systems, including those of humans, as structural and catalytic components of proteins and enzymes. However, the excessive accumulation of heavy metals in the environment constitutes a health risk for humans. Notably, Cd, Pb, As, and Hg are endocrine-disrupting chemicals [6]. For instance, excessive levels of cadmium in the human body cause high blood pressure and cardiovascular and cerebrovascular diseases [7,8]. Lead is the most pernicious heavy metal and can damage human brain cells, affecting the intellectual development of children and causing dementia in the elderly [9,10]. Arsenic can affect skin pigmentation and lead to abnormal keratinization [11,12]. Mercury directly accumulates in the liver when it is ingested by humans, causing damage to the brain and nervous system and affecting vision [13]. Therefore, it is

necessary to evaluate the health risk of heavy metals to humans, a topic that is of major societal concern and has attracted much research attention.

Yang et al. [14] evaluated the degree of heavy metals pollution and the resulting health risk in the Huayuan mining area of Hunan Province, and reported that the concentrations of Pb, Zn, and Cd exceeded the safe background levels determined by the State Environmental Protection Administration of Standard for risk control of soil pollution in agricultural land of soil environmental quality (GB 15618-1995) [15]. It was suggested that Pb and Cd posed a substantial health risk to residents via the consumption of vegetables from local agricultural lands. Chen et al. [16] assessed the health risks of heavy metals pollution in the Longxi lead–zinc mining area of Fujian Province. Fang et al. [17] used a single factor index and the Nemerow integrated pollution index to analyze the pollution levels of heavy metals in agricultural soil in Lin'an City in Hangzhou, and found that the degree of Pb pollution was moderate, while for Cd, Cu, and Zn it was slight, and that 160 samples were contaminated to a certain extent.

The northern piedmont of Mount Wutai in Shanxi Province has important iron ore reserves that are mined, and in addition there are scattered gold mines. The local soil environment has been seriously damaged as a result of large-scale mining activities, and human health has been affected. However, little attention has been paid to determining the possible levels of heavy metals pollution in agricultural soils in the region and the resulting health risks. Consequently, we collected 29 samples of agricultural soil from different locations in the area with the aim of analyzing the spatial distribution of the concentrations of heavy metals (Cd, Pb, As, and Hg). In order to determine the risk to human health we analyzed the data using determinations of the single factor pollution index (SFPI) and the Nemerow integrated pollution index, and we also applied the health risk assessment model developed by the United States Environmental Protection Agency (USEPA) [18–21]. It was hoped that the results would provide a scientific basis for the implementation of a regulatory policy by the government.

2. Materials and Methods

2.1. Study Site and Sampling

The study area is the northern piedmont of Mount Wutai, which is in the northeast part of Shanxi Province in China (113°10' to 114°00'E and 39°00' to 39°15'N). The upper reaches of the Hutuo River lie to the north; the Yedoufeng peak of Beitai Mountain lies to the south; and the towns of Yuli and Shentangbao are situated to the west and east, respectively (Figure 1). The landscape of the area is dominated by mountains with elevations up to ~3000 m, and therefore the soil types exhibit a distinct vertical zonation. The following soil types occur in the region, with decreasing altitude: subalpine meadow soil, montane meadow soil, mountain grassland meadow soil, brown soil–brown loam soil, leached cinnamon soil, calcareous cinnamon soil, and cinnamon soil. The geological structure of the study area is complex and the region has undergone multiple tectonic movements, which has resulted in mineralization, with metamorphic iron ores being abundant and widely distributed [22,23]. A large number of industrial and mining enterprises have developed in the area that have resulted in the accumulation of pollutants in the soil via wind transport and surface runoff.

Figure 1. Location of the study area in Shanxi Province (left) and location of soil sampling (right).

2.2. Sample Collection and Measurement of Heavy Metal Concentrations

Twenty-nine sampling sites were selected in different agricultural areas in the Mount Wutai area and samples were collected in June 2017. The sites were in agricultural fields located close to the iron ore mining plants near the Yukou River, E River, Yangyan River, and Qingyang River. Samples were taken using the ‘Plum Blossom arrangement’, which is suitable for small plots, flat terrain, and urban areas with a uniform degree of pollution. In each sampling point, five subsamples of approximately 500 g were collected and mixed to obtain composite soil samples. The top 0–20 cm of the soil layer was sampled. At the same time, the location and environmental characteristics of each sampling site were recorded in detail. In the laboratory, the soil samples were spread over a polyethylene sheet, air-dried at room temperature for two weeks, ground to a fine powder in a grinding rod swing mill, sieved through a 0.15-mm polyethylene sieve and homogenized to remove stones and plant roots. All the soil was kept in scaled plastic bags until analysis.

All samples received pretreatment and preparation of a standard solution and were measured in the Taiyuan Testing Center of the Ministry of Land and Resources, Shanxi Province according to the National Soil Quality standard (GB15618-1995) [15] and the Modern Analysis methods of soil elements (1992) [24]. All reagents used were of analytical grade. Water used was secondary distilled water. As, Hg, Pb, and Cd (National Network of Standard Material Centers, 100 $\mu\text{g}\cdot\text{mL}^{-1}$) were multielemental standard solutions. Soil samples were digested using a mixture of HNO_3 (15 mL)– HCl (10 mL)– HF (10 mL)– HClO_4 (5 mL) for the determination of the total concentrations of Cd and Pb, while the As and Hg concentrations were determined after aqua regia (3:1 HCl (15 mL) and HNO_3 (5 mL)). The concentrations of Cd, Pb, As, and Hg were measured using XSERIES 2 ICP-MS (Thermo Fisher Scientific, USA). The monitoring range of ICP-MS is 3–250 amu, and the detection limit is ppt level [25]. Standard curves were plotted using the standard solution concentrations of Cd, Pb, As, and Hg measured by ICP-MS with correlation coefficients of 0.9999, 0.9998, 0.999, 0.9999, respectively. These met the requirements of inductively coupled plasma mass spectrometry for the determination of heavy metal elements in soils and sediments (HJ 803-2016) (correlation coefficients greater than 0.999). The detection limits were 0.003, 0.001, 0.006, 0.004 $\mu\text{g}\cdot\text{L}^{-1}$, respectively, meeting the detection requirements for metals. The indicators in their accuracy were within the standard substances (GSS-25, GSS-12) scope of uncertainty.

2.3. Determination of Heavy Metal Pollution Indices

2.3.1. Single Factor Pollution Index

The single factor pollution index (SFPI) is an effective method for evaluating the pollution level of heavy metals; however, it does not reflect overall pollution levels in a region [26]. The SFPI is calculated using the following equation:

$$P_i = \frac{C_i}{S_i} \quad (1)$$

where P_i is the pollution index of element i , C_i is the measured data for metal i and S_i is the soil background value. The heavy metals content of the soil in the Mount Wutai area measured in 1986 was used as the background value of the study (no iron ore mining installations were present before 1986). The values of Cd, Pb, As, and Hg were 0.104, 15.67, 8.90 and 0.07 mg·kg⁻¹, respectively [27].

2.3.2. Nemerow Integrated Pollution Index

The Nemerow integrated pollution index (NIPI) provides a comprehensive measure of the overall pollution level of a study area [28] and enables comparisons to be made between different regions. The index is calculated using the following equation [29]:

$$P_N = \sqrt{\left(\frac{(P_i)_{ave}^2 + (P_i)_{max}^2}{2} \right)} \quad (2)$$

where P_N is the soil pollution index, and $(P_i)_{ave}$ and $(P_i)_{max}$ are the average and maximum values of the pollution element i within a specific area, respectively. The classification criteria for assessment of the soil heavy metals pollution index are shown in Table 1 [30].

Table 1. Classification criteria for heavy metals pollution in soil.

Class	Pollution Index of Element I	Pollution Index of Soil	Pollution Class	Pollution Level
1	$P_i \leq 0.7$	$P_N \leq 0.7$	Secure	Clean
2	$0.7 < P_i \leq 1$	$0.7 < P_N \leq 1$	Alert	Unpolluted
3	$1 < P_i \leq 2$	$1 < P_N \leq 2$	Mild	Began to be polluted
4	$2 < P_i \leq 3$	$2 < P_N \leq 3$	Moderately	Moderately polluted
5	$P_i > 3$	$P_N > 3$	Heavy	Extremely polluted

2.4. Health Risk Assessment

Health risk assessment focuses on the possible effects of certain pollutants on human health after they reach a certain dose level, and it includes cancer risk and noncarcinogenic risk. According to the classification systems of the USEPA Integrated Risk Information System (IRIS) and the International Agency for Research on Cancer (IARC), Cd and As are chemical carcinogens, while Pb and Hg are noncarcinogenic chemicals [31–33].

2.4.1. Exposure Assessment

Heavy metals in soils are transferred to the human body mainly via ingestion, inhalation, and dermal contact by hand and mouth [28,34,35]. The following equations are used to calculate the level of human exposure to heavy metals based on average daily intake (mg·kg⁻¹·day⁻¹) by a given route:

$$ADD_{ing} = \frac{c \cdot IngR \cdot CF \cdot EF \cdot ED}{BW \cdot AT} \quad (3)$$

$$ADD_{inh} = \frac{c \cdot InhR \cdot EF \cdot ED}{PEF \cdot BW \cdot AT} \quad (4)$$

$$ADD_{\text{derm}} = \frac{c \cdot SA \cdot CF \cdot SL \cdot ABS \cdot EF \cdot ED}{BW \cdot AT} \quad (5)$$

$$ADD = ADD_{\text{ing}} + ADD_{\text{inh}} + ADD_{\text{derm}} \quad (6)$$

where ADD_{ing} , ADD_{inh} , and ADD_{derm} are the average daily intake of heavy metals via ingestion, inhalation, and dermal contact, respectively; c is the concentration of metals in the soil ($\text{mg} \cdot \text{kg}^{-1}$); IngR is the ingestion rate ($\text{mg} \cdot \text{day}^{-1}$); CF is a conversion factor ($\text{kg} \cdot \text{mg}^{-1}$); EF is the exposure frequency ($\text{day} \cdot \text{yr}^{-1}$); ED is the exposure duration (yr); BW is the body weight of the exposed individual (kg); AT is the average exposure time for noncarcinogenic effects (day); InhR is the inhalation rate ($\text{m}^3 \cdot \text{day}^{-1}$); PEF is the particle emission factor ($\text{m}^3 \cdot \text{kg}^{-1}$); SA is the exposed skin area (cm^2); SL is the skin adherence factor ($\text{mg} \cdot (\text{cm}^2 \cdot \text{day})^{-1}$); and ABS is the dermal absorption factor (dimensionless). The value of each parameter is compared with the results of previous studies and with the actual conditions of Chinese residents [36,37], enabling suitable exposure parameters to be determined (Table 2).

Table 2. Definition and reference values of some parameters for health risk assessment.

Parameter	Value		Data Source
	Adults	Children	
Ingestion Rate ($\text{mg} \cdot \text{day}^{-1}$)	100	200	United States Environmental Protection Agency (USEPA)
Inhalation Rate ($\text{m}^3 \cdot \text{day}^{-1}$)	20	7.65	USEPA
Conversion Factor ($\text{kg} \cdot \text{mg}^{-1}$)	10^{-6}	10^{-6}	USEPA
Exposure Frequency ($\text{day} \cdot \text{yr}^{-1}$)	350	350	USEPA
Exposure Duration (yr)	24	6	USEPA
Exposed Skin Area (cm^2)	5145	2670	[36,37]
Skin Adherence Factor ($\text{mg} \cdot (\text{cm}^2 \cdot \text{day})^{-1}$)	0.07	0.2	USEPA
Dermal Absorption Factor	0.001	0.001	USEPA
Particle Emission Factor ($\text{m}^3 \cdot \text{kg}^{-1}$)	1.36×10^9	1.36×10^9	USEPA
Body Weight of the Exposed Individual (kg)	56.8	15.9	[36,37]
Average Exposure Time (day)	$ED \times 365^*$	$ED \times 365^*$	USEPA
	$70 \times 365^{**}$	$70 \times 365^{**}$	

Note: * noncarcinogenic absorption time; ** carcinogenic absorption time

2.4.2. Health Risk Characterization Assessment

A model of carcinogenic and noncarcinogenic health risk assessment is defined as follows [18,38,39]:

$$HQ_i = \sum_{j=1}^3 \frac{ADD_{ij}}{RfD_{ij}} \quad (7)$$

$$HI = \sum_{i=1}^4 HQ_i \quad (8)$$

$$CR_i = \sum_{j=1}^3 ADD_{ij} \cdot SF_{ij} \quad (9)$$

$$TCR = \sum_{i=1}^2 CR_i \quad (10)$$

where i is a heavy metal; j represents the three pathways described above; HQ is the hazard quotient, which is typically used to characterize noncarcinogenic hazards; HI is the hazard index, which is used to assess the overall potential for noncarcinogenic effects posed by more than one chemical; RfD is the reference dose, which is an estimate of the maximum permissible risk to human populations through

daily exposure ($\text{mg} \cdot (\text{kg} \cdot \text{day})^{-1}$); and CR and TCR are the carcinogenic risk and total carcinogenic risk, respectively, which are the probability that an individual will develop any type of cancer over a lifetime of exposure to carcinogenic hazards. For carcinogenic risk, the slope factor (SF) is used to directly convert the estimated daily intake of a toxin averaged over a lifetime of exposure to the incremental risk of an individual developing cancer. If the HQ or HI are less than 1, the exposed population is unlikely to experience obvious adverse health effects, while if HQ or HI are greater than one, then the value indicates the probability of adverse health effects [18,20,40]. These results were evaluated with reference to China's guidelines for site environmental assessment (DB11/T 656-2009) and research results from both China and elsewhere [39,41] (Table 3).

Table 3. Reference doses for noncarcinogenic metals and slope factors for carcinogenic metals.

Element	Reference Dose/ $\text{mg} \cdot (\text{kg} \cdot \text{day})^{-1}$			Slope Factor/ $(\text{kg} \cdot \text{day}) \cdot \text{mg}^{-1}$		
	Ingestion	Inhale	Dermal	Ingestion	Inhale	Dermal
Cd	1×10^{-3}	1×10^{-3}	12.4×10^{-5}	6.1	1.8×10^{-3}	6.1
Pb	3.5×10^{-3}	3.52×10^{-3}	5.25×10^{-4}	-	-	-
As	3×10^{-4}	1.23×10^{-4}	3×10^{-4}	1.5	4.3×10^{-3}	1.5
Hg	3×10^{-4}	3×10^{-4}	2.4×10^{-5}	-	-	-

3. Results and Analysis

3.1. Soil Heavy Metals Content and Spatial Distribution Characteristics

3.1.1. Soil Heavy Metals Content

The measured concentrations of the four heavy metals and their background values in the agricultural soils of the piedmont area of Mount Wutai are presented in Table 4. The soil in the study area was alkaline. The concentrations of the four heavy metals decreased in the following order: $\text{Pb} > \text{As} > \text{Hg} > \text{Cd}$ (with average values of 41.18, 16.05, 0.97, and $0.32 \text{ mg} \cdot \text{kg}^{-1}$, respectively). The concentration of Hg was the highest relative to the background value, and it exceeded the background level by a factor 13.84; the equivalent enrichment factors for Cd, Pb and As were 3.06, 2.63, and 1.80, respectively. The results of the application of the coefficient of variation analysis (CV) were classified as follows: high variation, $\text{CV} > 0.36$; intermediate variation, $0.16 < \text{CV} < 0.36$; low variation, $\text{CV} < 0.16$ [42]. For the studied agricultural soils, the values for all four elements exceeded 0.36, with the following values: Cd, 1.10; Pb, 0.75; As, 1.34; Hg, 2.47.

Table 4. Summary statistics of the heavy metals content of agricultural soil in the northern piedmont of Mount Wutai.

Analyzed value	Cd	Pb	As	Hg	pH
Average, $\text{mg} \cdot \text{kg}^{-1}$	0.32	41.18	16.05	0.97	8.03
• Range, $\text{mg} \cdot \text{kg}^{-1}$	0.088–1.804	4.65–138.21	1.31–108.51	0.018–13.4	
• SD	0.35	30.69	21.52	2.40	
• CV	1.10	0.75	1.34	2.47	
• Excess multiple	3.06	2.63	1.80	13.84	
Reference background ^a	0.104	15.67	8.90	0.070	

^a The reference background values were calculated based on Ma (1986) and references therein.

3.1.2. Spatial Distribution Characteristics of Heavy Metals

The method of inverse distance weighting was used to analyze the spatial distribution characteristics of heavy metals in the agricultural soils. As shown in Figure 2, Cd, Pb, and As had similar distributions, with low concentrations adjacent to the E River and values increasing away from the river on both sides. The Yangyan River had the highest concentrations, representing a serious

level of heavy metal pollution. The pollution levels were lower in the upper reaches of both the Yangyan River and Qingyang River, and they increased downstream, indicating that flowing water is an important agent in the transport and dispersion of heavy metals. The wastewater from ore dressing water contributes a lot to the heavy metals in suspended matter of the river and was an important carrier for heavy metal transport. The concentrations of Hg increase from the middle of the study area to both sides, with the highest values located in the eastern Qingyang River area, which reflects the size and number of iron ore locations. A few samples in the middle reach of the Yukou River exhibited relatively high concentrations of Hg, reflecting the influence of gold mining activity.

Figure 2. Cont.

Figure 2. Spatial distribution of heavy metals in agricultural soils of the Mount Wutai area.

3.2. Evaluation of Heavy Metals Pollution in Agricultural Soils of the Northern Piedmont of Mount Wutai

Substituting the measured heavy metals data into Equation (1) enabled the SFPI, P_i , to be obtained, and the results are listed in Table 5. The level of P_i heavy metals in the agricultural soils of the Mount Wutai can be ordered as: $Hg > Cd > Pb > As$. Notably, the level of pollution varied between different watersheds, which mainly reflects the distribution of mines and the scale of mining. There was a slight degree of Cd pollution in the E River; the Yukou River and Qingyang River were moderately polluted; and the Yangyan River was heavily polluted. The degree of Pb pollution in the Yukou River and E River was slight, while the Yangyan River and Qingyang River were heavily polluted. The Yukou River was slightly polluted, the E River and Qingyang River were at the alert level, and the Yangyan River was heavily polluted. The levels of Hg pollution were severe, and the values for the Qingyang River exceed the background by a factor greater than seven, indicating serious pollution.

Table 5. Heavy metals pollution index values for agricultural soils in the northern piedmont mining area of Mount Wutai.

Basin	Pi				P_N
	Cd	Pb	As	Hg	
Yukou River	2.0	1.88	1.34	6.72	5.20
E River	1.40	1.07	0.72	3.51	2.75
Yangyan River	6.52	4.45	4.29	8.93	7.63
Qingyang River	2.17	3.18	0.75	38.82	28.58
Mean	3.02	2.65	1.78	14.50	10.96

According to the NIPI, the comprehensive pollution index value was higher by a factor of 10.96 than the highest grading standard, indicating serious pollution levels. Among these values, the Qingyang River basin was as high as 28.58, which exceeds the grading standard by a factor of 9, indicating severe pollution. The equivalent factors for the Yangyan River and the Yukou River basin were 7.63 and 5.20, respectively, indicating relatively serious heavy metals pollution. The lowest comprehensive pollution index for the E River was 2.75, which indicates moderate pollution.

3.3. Human Health Risk Assessment

3.3.1. Exposure Risk Model

Based on the parameters of the health risk assessment method and the measured values of the heavy metals, the average daily exposure of adults and children to the four heavy metals could be obtained (Table 6). As shown in Table 6, the average daily exposure of adults to Cd, Pb, As and Hg were 1.86×10^{-7} , 8.00×10^{-5} , 9.31×10^{-6} , and 1.64×10^{-6} $\text{mg} \cdot (\text{kg} \cdot \text{day})^{-1}$, respectively, and the average daily exposures of children were 3.31×10^{-7} , 4.98×10^{-4} , 1.66×10^{-5} , and 1.16×10^{-5} $\text{mg} \cdot (\text{kg} \cdot \text{day})^{-1}$,

respectively. The average daily exposure of children was higher than that of adults, which is mainly related to the low degree of immunity of children and the greater chance of contact with soil during outdoor activities. The higher degree of daily exposure risk for children than for adults is similar to the results obtained for Yangmin and Chefei [19,43]. Compared with adults, the average daily exposure of children to the four heavy metals via the hand–mouth pathway was higher. The average daily exposure of children to Cd and As via the inhalation pathway was lower than in adults, and for Pb and Hg it was higher in children than in adults. Children’s daily exposure to heavy metals via skin contact was higher than in adults. Among the different exposure pathways, ingestion was the main route, followed by dermal contact, while heavy metals exposure via inhalation was less harmful to human health.

Table 6. Daily average exposure of the human body to heavy metals in agricultural soils in the northern piedmont of Mount Wutai ($\text{mg} \cdot (\text{kg} \cdot \text{day})^{-1}$).

Statistic		Cd	Pb	As	Hg
ADD _{ing}	Adult	1.84×10^{-7}	6.95×10^{-5}	9.28×10^{-6}	1.64×10^{-6}
	Children	3.30×10^{-7}	4.97×10^{-4}	1.66×10^{-5}	1.16×10^{-5}
ADD _{inh}	Adult	2.71×10^{-11}	1.02×10^{-8}	1.36×10^{-9}	2.40×10^{-10}
	Children	9.27×10^{-12}	1.40×10^{-8}	4.67×10^{-10}	3.29×10^{-10}
ADD _{derm}	Adult	6.64×10^{-10}	2.50×10^{-7}	3.35×10^{-8}	5.89×10^{-9}
	Children	8.79×10^{-10}	1.33×10^{-6}	4.43×10^{-8}	3.11×10^{-8}
ADD	Adult	1.86×10^{-7}	8.00×10^{-5}	9.31×10^{-6}	1.64×10^{-6}
	Children	3.31×10^{-7}	4.98×10^{-4}	1.66×10^{-5}	1.16×10^{-5}

3.3.2. Health Risk Assessment

The results of the risk assessment are listed in Table 7. For noncarcinogenic risk, Cd, Pb, As, and Hg had values of HQ and HI that were less than 1, indicating there was no health risk. Children have a higher risk of intake than adults via the hand–mouth pathway [44], making HI more important for children than for adults; this is in accord with the results of Li et al. (2008) [45]. The cancer risk of As and Cd exposure indicates higher values of CR and TCR for both adults and children, than the soil standard recommended by the USEPA ($10^{-6}/\text{yr}$) [18,38], but lower than the acceptable risk value defined by the USEPA (10^{-6} – $10^{-4}/\text{yr}$) [46–48]; however, the carcinogenic risk reached a higher level, which deserves more attention. For children, the carcinogenic risk of As and Cd was higher than for adults, with TCR indexes of 1.52×10^{-5} and 2.70×10^{-5} , respectively. The individual carcinogenic risk of As exposure is higher than the total carcinogenic risk, with values of 1.39×10^{-5} and 2.50×10^{-5} , respectively; these values were two orders of magnitude lower than the risk indexes for Cd, which are 1.26×10^{-6} and 2.01×10^{-6} , respectively. As appears to be the largest contributor to carcinogenic risk.

Table 7. Noncarcinogenic risk index and carcinogenic risk in adults and children in the northern piedmont of Mount Wutai.

Element	Hazard Quotient		Carcinogenic Risk	
	Adults	Children	Adults	Children
Cd	1.89×10^{-4}	3.20×10^{-4}	1.26×10^{-6}	2.01×10^{-6}
Pb	2.04×10^{-2}	1.45×10^{-1}	N.A.	N.A.
As	3.10×10^{-2}	5.52×10^{-2}	1.39×10^{-5}	2.50×10^{-5}
Hg	5.75×10^{-3}	4.00×10^{-2}	N.A.	N.A.
Hazard Index	5.73×10^{-2}	2.41×10^{-1}	-	-
Total Carcinogenic Risk	-	-	1.52×10^{-5}	2.70×10^{-5}

N.A.: Pb and Hg are noncarcinogenic heavy metals without SF data.

4. Discussion and Conclusions

This study demonstrated that the concentrations of Cd, Pb, As, and Hg in agricultural soils in the Mount Wutai area of Shanxi Province were all higher than the background values; in addition, their spatial distributions were similar. The pH was an important factor affecting the adsorption of heavy metals. Higher pH was favorable for adsorption of heavy metals. Hg, which was located around the Qingyang River basin in the eastern part of the study area, exhibited higher values than in other parts of the world, which may be related to the presence of large-scale gold mining activity in the Shahe Town–Dayingkou area in Fanshi County. The method of mixed-mercury extraction results in the release of a large amount of volatile mercury to the atmosphere, and, especially in winter, it accumulates downwind of the gold mining area [49,50] in the Qingyang River basin. The spatial distributions of Cd, Pb, and As can be summarized as follows: the E River, located in the middle of the country, had the lowest levels, while the Yukou River in the west and the Yangyan River in the east had the highest levels. This distribution is related to the degree of development of iron ore mining, transportation, and the living habits of people in different river basins. The E River is relatively long and the number of mining sites and tailing reservoirs is relatively small. It is relatively less affected by the three main types of waste (waste gases, wastewater, and waste residues). The reaches of the Yukou River, Yangyan River, and Qingyang River, however, are short, and there is a greater degree of industrial and mining activity in the basin. At the mining sites, abandoned slag, derelict machinery, and tailing reservoirs produced as a result of mining are the main causes of heavy metals pollution in the vicinity of mine sites. In the process of adsorption kinetics, the physical and chemical properties and material composition and characteristics all affect the adsorption of heavy metals by soil.

Greater traffic volume in mining areas contributes to high Pb concentrations [48,51]. High Cd levels were mainly the result of the accumulation of acidic wastewater and waste discharges from iron ore mining [52–54]. In health risk assessment, the total daily average absorption risk for the four heavy metals indicated that children had a higher health risk than adults. Of the four metals, Cd had less health risk for children via respiratory intake, mainly because children have a lower respiratory rate; in contrast, As and Hg posed a greater health risk for adults than children due to their greater body weight and longer duration of absorption. For noncarcinogenic health risks, the levels of the four heavy metals are not significant. For carcinogenic risk, As was the main carcinogenic factor, which may be related to wastewater, waste residue, or tailing pond discharge during iron ore mining; it readily accumulates in agricultural soil via fluvial transportation and wet–dry deposition. In addition, the degree of As pollution is also affected by the living habits of local peoples and by farming practices.

As a result, Hg was present at the highest levels relative to the background, and this result is consistent with Marin Senila et al. (2012) [55]. Calculation of NIPI values indicated that the northern piedmont is seriously polluted, with the pollution levels of individual river basins in the following order: Qingyang River > Yangyan River > Yukou River > E River. This trend is likely related to the number and scale of iron ore and gold mining activities. The health risk of exposure to heavy metals

is higher for children than for adults. Hand–mouth intake is the main pathway for heavy metals to enter the human body, followed by skin contact. None of the four heavy metals had a noncarcinogenic health risk. Carcinogenic health risk assessment indicated that As and Cd present a higher cancer risk and that the cancer risk for children is higher than for adults. The studied agricultural soils were seriously affected by heavy metals pollution, posing a potentially serious hazard to the health of local inhabitants, which should be noted by the relevant administrative bodies. Government departments need to formulate appropriate policies and regulations to reduce risks, and mining activities should be strictly controlled.

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