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Human Health Risk Assessment and Safety Threshold of Harmful Trace Elements in the Soil Environment of the Wulantuga Open-Cast Coal Mine

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Received: 6 September 2015; Accepted: 20 November 2015; Published: 30 November 2015
Academic Editors: Shifeng Dai and David Cliff

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Abstract: In this study, soil samples were collected from a large-scale open-cast coal mine area in Inner Mongolia, China. Arsenic (As), cadmium (Cd), beryllium (Be) and nickel (Ni) in soil samples were detected using novel collision/reaction cell technology (CCT) with inductively-coupled plasma mass spectrometry (ICP-MS; collectively ICP-CCT-MS) after closed-vessel microwave digestion. Human health risk from As, Cd, Be and Ni was assessed via three exposure pathways—inhalation, skin contact and soil particle ingestion. The comprehensive carcinogenic risk from As in Wulantuga open-cast coal mine soil is 6.29–87.70-times the acceptable risk, and the highest total hazard quotient of As in soils in this area can reach 4.53-times acceptable risk levels. The carcinogenic risk and hazard quotient of Cd, Be and Ni are acceptable. The main exposure route of As from open-cast coal mine soils is soil particle ingestion, accounting for 76.64% of the total carcinogenic risk. Considering different control values for each exposure pathway, the minimum control value (1.59 mg/kg) could be selected as the strict reference safety threshold for As in the soil environment of coal-chemical industry areas. However, acceptable levels of carcinogenic risk are not unanimous; thus, the safety threshold identified here, calculated under a 1.00×10^{-6} acceptable carcinogenic risk level, needs further consideration.

Keywords: carcinogenic risk; hazard quotient; open-cast coal mine; arsenic; soil; safety threshold; harmful trace elements

1. Introduction

Coal will continue to play an important role in the global energy supply, especially in China, for a long time to come [1], and will make significant contributions to the development of human society and the standards of living. However, some harmful trace elements, such as arsenic (As), cadmium (Cd), beryllium (Be) and nickel (Ni) are enriched in coal [2,3] with the accompanying minerals. Researchers observed that As and Hg (mercury) was hosted in pyrite, Be and U (uranium) adsorbed in clay minerals and, meanwhile, F (fluorine) enriched with kaolinite [4–6], through the effect of sedimentary diagenesis, microbial action, tectonism, magmatic hydrothermal activity or groundwater activity [7–9]. These trace harmful elements, in various forms may migrate into soil, groundwater, air and other environmental media [10] and negatively affect human health, through natural activities, such as hydrothermal activity, or human activities, like coal gasification or coal coking processes.

Chemicals, such as heavy metals, have been shown to cause human cancers [11]. As, Cd, Be, Ni and other harmful trace compounds found in coal, which conspicuously cause toxicity in humans, were documented and suggested by the U.S. Environmental Protection Agency (U.S. EPA) [12], as well as by the Ministry of Environmental Protection of the People's Republic of China [13]. Studies on the level of their risk to human health and corresponding risk control in the mining process are important for the safety and health of workers and residents in mining areas.

Health risk assessment [14] is a comprehensive evaluation method that links environmental pollution and human health [15]. Environmental risk assessment in China was started in the 1980s, and human health risk evaluation studies were developed in the 1990s. Based on the assessing processes and models used in different countries, software was developed for the assessment of health and the environmental risks of contaminated sites in China, named the Health and Environmental Risk Assessment (HERA) [16], and this software was applied to the assessment of contaminated sites, such as the areas surrounding oilfields or other chemical plants. In recent years, the human health risk caused by As, Cd, Be and other toxic trace elements in some sites was quantitatively evaluated using different methods of health risk assessment. Juhasz *et al.* [17] evaluated the human health risk of As in rice; the results indicated that different forms of As could cause different levels of risk to human health. Zhuang *et al.* [18] assessed the human health risk of Pb and Cd in the Huayuan mining area in China, and results indicated that Pb and Cd accumulated in vegetables had severe potential risks for human health. Ren *et al.* [19] evaluated the potential risk of Pb in the soil environment for children in Shenyang city, and Li *et al.* [20] calculated the health risk level caused by Cd, Cu and Se in rice grain in the Nanjing area.

Although there were several models and standards for human health risk assessment, both in China and globally, and several health risk assessments were carried out, research on health risk assessment of harmful trace elements in open-cast coal mines is still very limited. Considering the ecological system properties of the open-cast mining area in the northwest of China and the complex contamination characteristics of multiple trace elements, this study could be a useful complement in this field. Furthermore, this study aims to propose safety thresholds for harmful trace elements (As, Cd, Be and Ni) in the coal mine area, which has implications for the protection of workers and industry health. We comprehensively compared mainstream evaluation models and methods, such as CLEA (Contaminated Land Exposure Assessment [21,22]), RBCA (Risk-Based Corrective Action [23,24]) and HERA (Health and Environmental Risk Assessment [16]). This study used Chinese standard technical guidelines for risk assessment of contaminated sites (HJ25.3-2014) [25] to carry out human health risk assessment of harmful trace elements in the Wulantuga open-cast coal mine area.

2. Experimental Section

2.1. Sample Collection

Soil samples were collected from the Wulantuga coal mine area, which is located in Xilinhaote in Inner Mongolia (north latitude 43°56′57.86″ and east longitude 115°54′37.36″ in China) in July 2014. Soil samples were collected using a geotome for a 0–15-cm depth of each layer, and in each layer, three sampling points were set. The soil samples were stored in plastic sealing bags and stored in a portable freezer until they were returned to the laboratory. The Wulantuga open-cast coal mine is still in operation; the area where the coal mine is located has an annual average temperature of 0–3 °C. The average annual rainfall was less than 300 mm, with a perennial southwest wind. Proven coal reserves were 760 million tons; the annual output is 7.3 million tons, and 337 staff work here. Many scholars have studied the geochemistry and mineralogy of the coal deposit in this coal mine [26–29]. The open-cast coal mine and the sampling sites are illustrated in Figure 1, and the distribution of sampling points and soil profile information is shown in Figure 2. Background soil samples were taken from a grassland, which was about 15 km away from Xilinhaote city in the northeast direction.

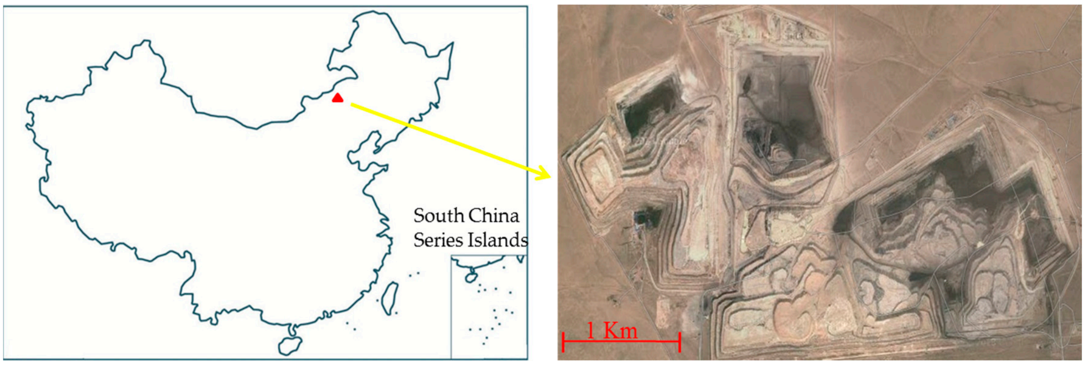


Figure 1. Location of the Wulantuga coal mine.

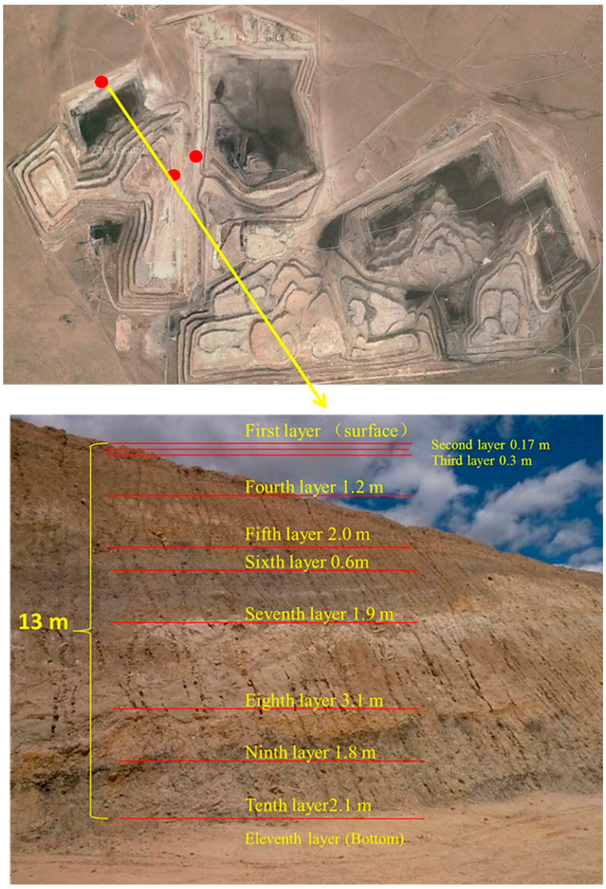


Figure 2. The distribution of sampling points and sections in the mining area.

2.2. Sample Handling and Detection

After drying the soil samples in an oven for 8 h at 105 °C [30], they were crushed to 200 mesh. The samples were digested in an UltraCLAVE microwave high-pressure reactor (Milestone, Milano, Italy) for 175 min [31]. Next, 50 mg of the soil sample were digested in 5 mL 40% HF, 2 mL 65% HNO_3 and 1 mL 30% H_2O_2. Initial nitrogen pressure was set at 50 bars. The heating process is: 12 min to 60 °C, 20 min to 125 °C, 8 min to 160 °C, 15 min to 240 °C, 60 min to 240 °C. [31]. Inductively-coupled plasma mass spectrometry (ICP-MS, ThermoScientific Xseries 2, Thermo Fisher Scientific, Waltham, MA, USA) was used to determine the amounts of the trace elements (plasma RF power set to 1400 W, sampling depth set to 130 steps, peristaltic pump speed set to 30 RPM, collision gas flow set to 4 mL/min, dwell time set to 10 ms, peak jumping acquisition mode, nebulizer gas flow set to 1.00 L/min, auxiliary gas flow set to 0.80 L/min, cool gas flow set to 13.00 L/min). The linearity of the calibration curves was considered acceptable in the range 0–100 μg/L with a determination coefficient $r^2 > 0.9999$. The method detection limit (MDL) of these elements was about 0.02 μg/L. As was determined using ICP-MS with collision cell technology (CCT) due to its volatility. Polyfluoroalkoxy volumetric flasks were used without drying on an electric hot plate to avoid volatile loss. A laser particle size analyzer was used to determine the texture of the soil samples.

2.3. Health Risk Assessment Methods

2.3.1. Exposure Assessment

During the preliminary stage of this study, Co (cobalt), Hg, Cu (copper), Zn (zinc), Se (selenium) and U concentrations were found to be low and not considered to be potential human health risks, and there were no effective toxicity parameters of Cr (chromium) and Pb (plumbum). Therefore, we selected As, Cd, Be and Ni as the major elements to evaluate. Different land use patterns define the land type, for example residential, cultural and school land are defined as sensitive sites. Industrial lands are defined as non-sensitive sites. As the experimental site is a typical non-sensitive site, the ways in which human health could be influenced in this coal mining area were identified according to the recommended guidelines for human health risk assessment of contaminated sites [25]. Considering that there was no surface water in the area surrounding the mine, the groundwater was not used for drinking and based on published reports [32–35], three routes of exposure—inhalation of particles, skin contact and ingestion of soil particles—were selected to evaluate the human health risk of this mining area. The formulas by which corresponding soil exposure doses of the three exposure ways were calculated are listed in Table 1.

Table 1. Calculating models of soil exposure dose in three soil exposure pathways.

Exposure Routes	Instruction	Formula for Calculation of Exposure Dose	Equation Number
Inhalation of particles	Carcinogenic risk	$OISER_{ca} = \frac{OSIR_a \times ED_a \times EF_a \times ABS_0}{BW_a \times AT_{ca}} \times 10^{-6}$	(1)
	Non-carcinogenic risk	$OISER_{nc} = \frac{OSIR_a \times ED_a \times EF_a \times ABS_0}{BW_a \times AT_{nc}} \times 10^{-6}$	(2)
Skin contact	Carcinogenic risk	$DCSER_{ca} = \frac{SAE_a \times SSAR_a \times EF_a \times ED_a \times E_V \times ABS_d}{BW_a \times AT_{ca}} \times 10^{-6}$	(3)
	Non-carcinogenic risk	$DCSER_{nc} = \frac{SAE_a \times SSAR_a \times EF_a \times ED_a \times E_V \times ABS_d}{BW_a \times AT_{nc}} \times 10^{-6}$	(4)
Ingestion of soil particles	Carcinogenic risk	$PISER_{ca} = \frac{PM_{10} \times DAIR_a \times ED_a \times PIAF \times (fspo \times EFO_a + fspi \times EFI_a)}{BW_a \times AT_{ca}} \times 10^{-6}$	(5)
	Non-carcinogenic risk	$PISER_{nc} = \frac{PM_{10} \times DAIR_a \times ED_a \times PIAF \times (fspo \times EFO_a + fspi \times EFI_a)}{BW_a \times AT_{nc}} \times 10^{-6}$	(6)

The main parameters of the contaminated site risk-assessment model include concentration and toxicological parameters of the pollutants, site condition parameters and exposure parameters. The values of each concentration of the target pollutants and the site condition parameters were measured. The exposure factor parameters were applied without considering the exposure of children, based on the non-sensitive properties of the coal mining area in this paper (Table 2).

2.3.2. Toxicological Evaluation

Based on the parameter value selection and the calculation of the various exposure routes, the carcinogenic risk and hazard quotient were calculated using the formulas and parameters listed in Tables 2 and 3. Then, the comprehensive human health risk was summed up with the individual risk associated with each exposure route [25]. The specific level of human health risk for each sampling point thus obtained was compared to the acceptable level of human carcinogenic risk (1.00×10^{-6}) and hazard quotient (with the standard value of 1.00) [25,35].

CR_{ois} is the carcinogenic risk associated with the exposure route of the inhalation of particles (dimensionless); CR_{dcs} is the carcinogenic risk associated with the exposure route of skin contact (dimensionless); CR_{pis} is the carcinogenic risk associated with the exposure route of the ingestion of soil particles (dimensionless); HQ_{ois} represents the hazard quotient associated with the exposure route of the ingestion of soil particles (dimensionless); HQ_{dcs} is the hazard quotient associated with the exposure route of skin contact (dimensionless); HQ_{pis} is the hazard quotient associated with the exposure route of the ingestion of soil particles (dimensionless). The remaining parameters are shown in Table 2.

Table 2. Major parameters in the exposure dose calculation models.

Parameter	Implication	Value	Unit
$OSIR_a$	Intake amount of soil per day	100.00	$mg \cdot day^{-1}$
ED_a	Exposure time	25.00	a
EF_a	Exposure rate	250.00	$day \cdot a^{-1}$
BW_a	Weight of an adult	56.80	kg
ABS_0	Absorption efficiency factor of inhaled particles	26,280.00	-
AT_{ca}	Average carcinogenic effect time	26,280.00	day
AT_{nc}	Average non-carcinogenic effect time	91,280.00	day
SAE_a	Exposed skin area	2854.62	cm^2
$SSAR_a$	Soil adhesion coefficient of skin surface	0.20	$mg \cdot cm^{-2}$
ABS_d	Absorption efficiency factor of skin contact	0.03	-
E_V	Frequency of skin contact per day	1.00	$time \cdot day^{-1}$
PM_{10}	Concentration of inhalable suspended particulate matter	0.15	$m^3 \cdot day^{-1}$
$DAIR_a$	Air intake per day	14.50	$m^3 \cdot day^{-1}$
PIAF	Retention ratio of inhalable soil particles *in vivo*	0.75	-
fspi	Proportion of soil particles in indoor air	0.80	-
fspo	Proportion of soil particles in outdoor air	0.50	-
EFI_a	Indoor exposure frequency	187.50	$day \cdot a^{-1}$
EFO_a	Outdoor exposure frequency	62.50	$day \cdot a^{-1}$
C_{sur}	Concentration of pollutants in the surface soil	Table 6	$mg \cdot kg^{-1}$
SF_0	Oral intake slope factor of carcinogenic element	1.50	$(mg/kg \cdot day)^{-1}$
SF_d	Skin contact slope factor of carcinogenic element	1.00	$(mg/kg \cdot day)^{-1}$
SF_i	Breathing slope factor of carcinogenic element	4.30	$(mg/kg \cdot day)^{-1}$
SAF	Reference dose distribution coefficient of soil exposure	0.20	-
RfD_0	Reference dose for ingestion	3.00×10^{-4}	$mg \cdot kg^{-1} \cdot day^{-1}$
RfD_d	Reference dose for skin contact	3.00×10^{-4}	$mg \cdot kg^{-1} \cdot day^{-1}$
RfD_i	Reference dose for inhalation	3.83×10^{-6}	$mg \cdot kg^{-1} \cdot day^{-1}$

Table 3. Formulas for the calculation of carcinogenic risk and the hazard quotient.

Exposure Routes	Instruction	Cancer Risk or Hazard Quotient Calculating Formulas	Equation Number
Inhalation of particles	Carcinogenic risk	$CR_{ois} = OISER_{ca} \times C_{sur} \times SF_o$	(7)
	Hazard quotient	$HQ_{ois} = \frac{OISER_{nc} \times C_{sur}}{RfD_O \times SAF}$	(8)
Skin contact	Carcinogenic risk	$CR_{dcs} = DCSER_{ca} \times C_{sur} \times SF_d$	(9)
	Hazard quotient	$HQ_{dcs} = \frac{DCSER_{nc} \times C_{sur}}{RfD_d \times SAF}$	(10)
Ingestion of soil particles	Carcinogenic risk	$CR_{pis} = PISER_{ca} \times C_{sur} \times SF_i$	(11)
	Hazard quotient	$HQ_{pis} = \frac{PISER_{nc} \times C_{sur}}{RfD_i \times SAF}$	(12)

2.3.3. Calculation of Control Values

When carcinogenic risk exceeds the recommended safety value, the risk control value associated with the corresponding routes of exposure should be calculated (Table 4).

ACR refers to the acceptable level of human carcinogenic risk (1×10^{-6}, dimensionless); AHQ is the acceptable level of the hazard quotient (1, dimensionless). The remaining parameters are listed in Table 2.

Table 4. Formulas for the calculation of the safety threshold.

Exposure Routes	Instruction	Safety Threshold Formulas	Equation Number
Inhalation of particles	Carcinogenic risk	$RCVS_{ois} = \frac{ACR}{OISER_{ca} \times SF_0}$	(13)
	Hazard quotient	$HCVS_{ois} = \frac{RfD_0 \times SAF \times AHQ}{OISER_{nc}}$	(14)
Skin contact	Carcinogenic risk	$RCVS_{dcs} = \frac{ACR}{DCSER_{ca} \times SF_d}$	(15)
	Hazard quotient	$HCVS_{dcs} = \frac{RfD_d \times SAF \times AHQ}{DCSER_{nc}}$	(16)
Ingestion of soil particles	Carcinogenic risk	$RCVS_{pis} = \frac{ACR}{PISER_{ca} \times SF_i}$	(17)
	Hazard quotient	$HCVS_{pis} = \frac{RfD_i \times SAF \times AHQ}{PISER_{nc}}$	(18)

3. Results and Discussion

3.1. Harmful Trace Elements' Concentrations and Exposure Levels

The concentrations of As, Cd, Be and Ni in each sample and carcinogenic and non-carcinogenic exposure, cancer risk and the hazard quotient under each exposure pathway are provided in Tables 6 and 7. The distribution of As was between 7.67 and 107.07 mg/kg, whereas that of Cd, Be and Ni was 0.27–0.70, 1.73–4.85 and 11.75–37.09 mg/kg, respectively. The concentrations of As, Cd, Be and Ni in raw coal were 14.08, 0.05, 0.01 and 75.50 mg/kg, respectively. Carcinogenic exposure level of As in this area under the exposure pathway of the inhalation of particles was 4.19×10^{-7} m^3/day, whereas the non-carcinogenic exposure level of Cd, Be and Ni was 1.21×10^{-6} m^3/day. Carcinogenic exposure levels of As and Cd under the exposure pathway of skin contact in this area were 7.17×10^{-8} and 2.39×10^{-9} m^3/day, respectively, whereas the non-carcinogenic exposure levels were 2.06×10^{-7} and 6.88×10^{-9} m^3/day, respectively. The carcinogenic exposure level of As under the exposure pathway of the ingestion of soil particles in this area was 4.95×10^{-9} m^3/day, and the non-carcinogenic exposure level of Cd, Be and Ni was 1.43×10^{-8} m^3/day. The particle size of the soil samples is shown in Table 5. The texture of the soil from "10 m to the edge of the mine" was silty loam and from "200 m to the edge of the mine" sandy clay loam, and the other twelve soil samples were all sandy loam soil.

Table 5. Particle size of each soil sample.

Sampling Site	Percentage of Each Size (%)		
	<0.002 mm	0.02–0.002 mm	2–0.02 mm
Grassland	2.00	12.29	85.70
10 m to the edge of the mine	5.64	45.76	48.58
200 m to the edge of the mine	2.74	20.91	76.33
First layer	0.49	4.03	95.47
Second layer	1.15	10.15	88.68
Third layer	0.38	4.46	95.15
Fourth layer	1.32	8.56	90.11
Fifth layer	1.48	10.80	87.70
Sixth layer	0.97	6.94	92.07
Seventh layer	0.87	8.60	90.52
Eighth layer	1.09	8.11	90.79
Ninth layer	1.72	11.31	86.95
Tenth layer	0.52	7.04	92.43
Eleventh layer	0.92	7.38	91.69

Table 6. Concentrations and evaluation parameters of As under each exposure pathway.

Description	Sampling Site	Concentration of As (mg/kg)	Inhalation of Particles		Skin Contact		Ingestion of Soil Particles	
			CR	HQ	CR	HQ	CR	HQ
Background soil	Grassland	12.63	7.93×10^{-6}	2.60×10^{-1}	1.36×10^{-6}	4.00×10^{-2}	1.05×10^{-6}	2.40×10^{-1}
Mine side soil	10 m to the edge of the mine	66.10	4.15×10^{-5}	1.34	7.14×10^{-6}	2.30×10^{-1}	5.51×10^{-6}	1.24
	200 m to the edge of the mine	97.23	6.11×10^{-5}	1.96	1.05×10^{-5}	3.30×10^{-1}	8.11×10^{-6}	1.81
Section soil	First layer	13.67	8.59×10^{-6}	2.80×10^{-1}	1.48×10^{-6}	5.00×10^{-2}	1.14×10^{-6}	2.60×10^{-1}
	Second layer	10.56	6.63×10^{-6}	2.20×10^{-1}	1.14×10^{-6}	4.00×10^{-2}	8.81×10^{-7}	2.00×10^{-1}
	Third layer	7.67	4.82×10^{-6}	1.60×10^{-1}	8.29×10^{-7}	3.00×10^{-2}	6.40×10^{-7}	1.40×10^{-1}
	Fourth layer	47.97	3.01×10^{-5}	9.70×10^{-1}	5.18×10^{-6}	1.60×10^{-1}	4.00×10^{-6}	9.00×10^{-1}
	Fifth layer	107.07	6.72×10^{-5}	2.16	1.16×10^{-5}	3.70×10^{-1}	8.93×10^{-6}	2.00
	Sixth layer	47.45	2.98×10^{-5}	9.60×10^{-1}	5.12×10^{-6}	1.60×10^{-1}	3.96×10^{-6}	8.90×10^{-1}
	Seventh layer	11.39	7.15×10^{-6}	2.30×10^{-1}	1.23×10^{-6}	4.00×10^{-2}	9.50×10^{-7}	2.10×10^{-1}
	Eighth layer	32.94	2.07×10^{-5}	6.70×10^{-1}	3.56×10^{-6}	1.10×10^{-1}	2.75×10^{-6}	6.20×10^{-1}
	Ninth layer	20.71	1.30×10^{-5}	4.20×10^{-1}	2.24×10^{-6}	7.00×10^{-2}	1.73×10^{-6}	3.90×10^{-1}
	Tenth layer	14.21	8.92×10^{-6}	2.90×10^{-1}	1.54×10^{-6}	5.00×10^{-2}	1.19×10^{-6}	2.70×10^{-1}
	Eleventh layer	25.92	1.63×10^{-5}	5.20×10^{-1}	2.80×10^{-6}	9.00×10^{-2}	2.16×10^{-6}	4.80×10^{-1}

Annotation: CR represents carcinogenic risk; HQ represents hazard quotient.

Table 7. Concentrations and evaluation parameters of each exposure pathway for different elements.

Sample Description	Sampling Site	Concentration (mg/kg)			HQ of Inhalation of Particles			HQ of Skin Contact	HQ of Ingestion of Soil Particles		
		Cd	Be	Ni	Cd	Be	Ni	Cd	Cd	Be	Ni
Background soil	Grassland	0.73	2.02	25.92	4.44×10^{-3}	6.11×10^{-3}	7.85×10^{-3}	7.34×10^{-1}	2.06×10^{-2}	2.83×10^{-2}	8.08×10^{-2}
Mine side soil	10 m to the edge of the mine	0.40	3.71	24.13	2.42×10^{-3}	1.12×10^{-2}	7.31×10^{-3}	4.00×10^{-1}	1.12×10^{-2}	5.20×10^{-2}	7.52×10^{-2}
	200 m to the edge of the mine	0.38	3.08	22.71	2.32×10^{-3}	9.32×10^{-3}	6.88×10^{-3}	3.83×10^{-1}	1.07×10^{-2}	4.32×10^{-2}	7.08×10^{-2}
Section soil	First layer	0.43	1.73	22.92	2.61×10^{-3}	5.25×10^{-3}	6.94×10^{-3}	4.31×10^{-1}	1.21×10^{-2}	2.43×10^{-2}	7.14×10^{-2}
	Second layer	0.51	2.28	20.11	3.08×10^{-3}	6.92×10^{-3}	6.09×10^{-3}	5.09×10^{-1}	1.42×10^{-2}	3.20×10^{-2}	6.27×10^{-2}
	Third layer	0.33	3.85	20.61	1.98×10^{-3}	1.17×10^{-2}	6.25×10^{-3}	3.28×10^{-1}	9.18×10^{-3}	5.40×10^{-2}	6.42×10^{-2}
	Fourth layer	0.70	2.10	11.75	4.21×10^{-3}	6.38×10^{-3}	3.56×10^{-3}	6.96×10^{-1}	1.95×10^{-2}	2.95×10^{-2}	3.66×10^{-2}
	Fifth layer	0.54	3.18	37.09	3.30×10^{-3}	9.63×10^{-3}	1.12×10^{-2}	5.45×10^{-1}	1.53×10^{-2}	4.46×10^{-2}	1.16×10^{-1}
	Sixth layer	0.32	4.44	23.65	1.92×10^{-3}	1.35×10^{-2}	7.17×10^{-3}	3.17×10^{-1}	8.87×10^{-3}	6.23×10^{-2}	7.37×10^{-2}
	Seventh layer	0.27	2.70	18.52	1.61×10^{-3}	8.17×10^{-3}	5.61×10^{-3}	2.66×10^{-1}	7.46×10^{-3}	3.78×10^{-2}	5.77×10^{-2}
	Eighth layer	0.41	4.85	31.26	2.48×10^{-3}	1.47×10^{-2}	9.47×10^{-3}	4.11×10^{-1}	1.15×10^{-2}	6.80×10^{-2}	9.74×10^{-2}
	Ninth layer	0.45	2.50	18.55	2.75×10^{-3}	7.58×10^{-3}	5.62×10^{-3}	4.54×10^{-1}	1.27×10^{-2}	3.51×10^{-2}	5.78×10^{-2}
	Tenth layer	0.49	2.04	26.27	2.94×10^{-3}	6.19×10^{-3}	7.96×10^{-3}	4.86×10^{-1}	1.36×10^{-2}	2.87×10^{-2}	8.19×10^{-2}
	Eleventh layer	0.35	3.19	28.45	2.15×10^{-3}	9.65×10^{-3}	8.62×10^{-3}	3.55×10^{-1}	9.93×10^{-3}	4.47×10^{-2}	8.87×10^{-2}

3.2. Health Risk Assessment

3.2.1. Carcinogenic Risk

Regarding the harmful trace elements, carcinogenic risk of As was the most significant, whereas no obvious carcinogenic effect was observed for other elements. The variation of carcinogenic risk of As in each soil profile layer is illustrated in Figure 3. In the first few soil section layers, the carcinogenic risk level of As was lower, but still exceeded the recommended safety value (1×10^{-6}). Overall, it did not show an obvious change with increasing depth. A high carcinogenic risk value was observed at a depth of 1–7 m. The highest carcinogenic risk value observed was 8.77×10^{-5}, which is 87.70-times the recommended safety value. Therefore, it could be concluded that the carcinogenic risk level of As is high, which suggests that it is not safe for workers or other people to stay in this area for a long period. Therefore, it is necessary to adopt effective safety measures for the staff working in this open-cast coal mining area.

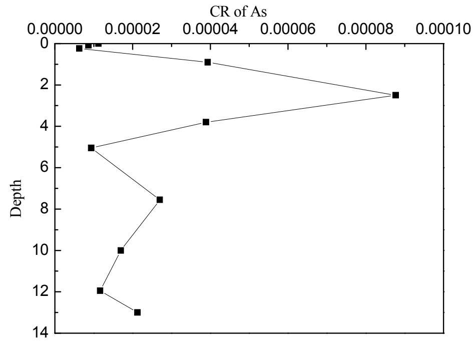
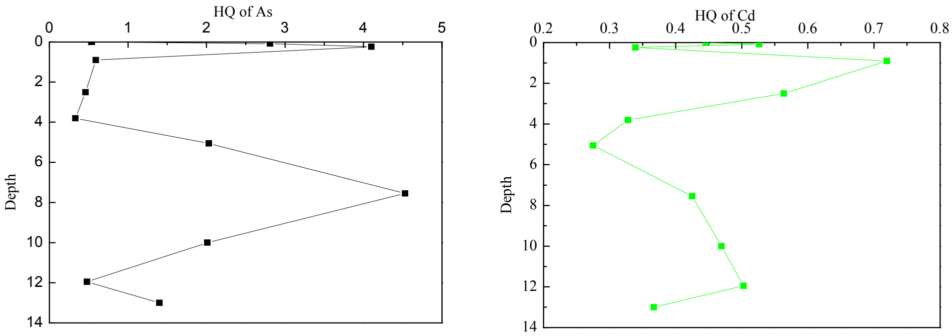


Figure 3. The carcinogenic risk level of As in each section layer.

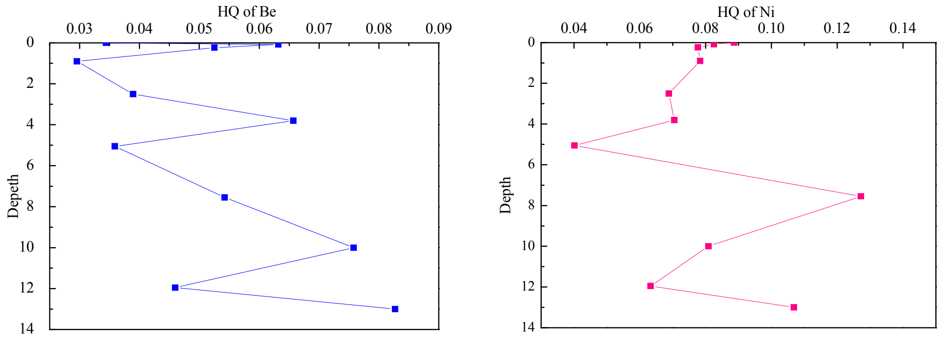
3.2.2. Hazard Quotient

The variation in the hazard quotient value of As, Cd, Be and Ni in each soil profile layer is illustrated in Figure 4. Among these, the hazard quotient of As was most prominent. Samples from three sampling points exceeded the recommended safety value under the exposure pathways of the inhalation of particles and the ingestion of soil particles. The highest value was 2.16-times the acceptable risk level, and the total hazard quotient of each exposure pathways was up to 4.70-times the acceptable risk level. Generally, the hazard quotients of other elements in each soil section layer were much lower; even the maximum value did not exceed the recommended safety value. Therefore, this study did not investigate the hazard quotients levels of those elements that were acceptable. However, because exploration of coal has been carried out for a long time in this area, the possibility of an increase in the hazard quotient with coal mine excavation should be studied.



(**a**) HQ of As (**b**) HQ of Cd

Figure 4. *Cont.*

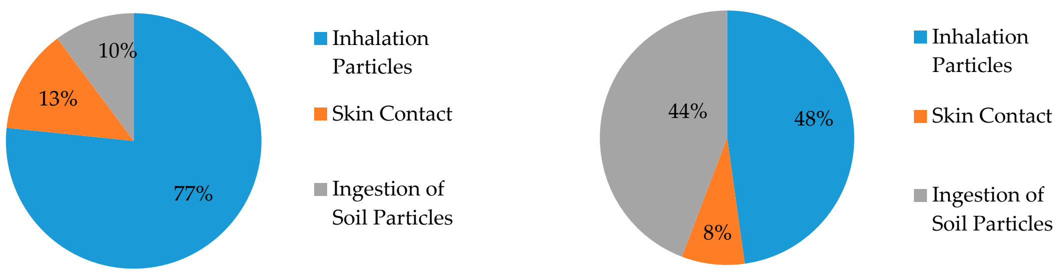


(**c**) HQ of Be (**d**) HQ of Ni

Figure 4. The hazard quotient (HQ) value of As, Cd, Be and Ni in each section layer and the changing trend.

3.2.3. Contribution of Different Exposure Pathways

In order to devise strategies for the mitigation and prevention of human health risk in coal mines, the contribution of different exposure pathways to human risk was calculated in this paper (Figure 5).



(**a**) (**b**)

Figure 5. The contribution of different exposure pathways to human health risk. (**a**) Carcinogenic risk; (**b**) Non-carcinogenic risk.

The carcinogenic risk of As by the inhalation of particles exposure pathway could reach 76.64% in this open-cast coal mining area (Figure 5). Inhalation of particles was also the most important exposure pathway for non-carcinogenic risk; the contribution of the ingestion of soil particles increased to 44.22%, and it can be concluded that different exposure pathways can have different contribution ratios when the damage type (carcinogenic risk or hazard quotient) is different. Additionally, in order to control and decrease the human health risk in the open-cast coal mining area, risk control should be aimed at blocking the main exposure pathway, specifically to prevent the inhalation of particles by workers, by advising them to wear safety masks.

3.3. Safety Threshold Identification

According to the human health risk assessment of the open-cast coal mine area, only the carcinogenic risk of As in each sampling point exceeded the acceptable standard level, so in this research, the risk control values of As under the corresponding routes of exposure were calculated, according to the method provided in Table 4; the calculation results are shown in Table 8. There are still three sampling points that exceed the recommended safety value under the exposure pathways of the inhalation of particles and the ingestion of soil particles, respectively. The risk control values of the two exposure pathways were also calculated (Table 2).

The risk control values of As in these open-cast coal mine soils varied among different exposure pathways. The lowest risk control value of arsenic is 1.59 mg/kg.

Table 8. Risk control value of arsenic in open-cast coal mine area soil.

Exposure Route	Type of Risk	Control Value (mg/kg)
Inhalation of particles	carcinogenic	1.59
Skin contact	carcinogenic	9.26
Ingestion of soil particles	carcinogenic	11.99
Inhalation of particles	non-carcinogenic	49.50
Ingestion of soil particles	non-carcinogenic	55.55

However, it should be noted that this open-cast coal mine is located in the northwest of China, which is windy and dry in most seasons; this leads to an abundance of dust and light soil particles. As a result, frequent inhalation of soil particles is unavoidable. Therefore, considering the principle of strict management for risk control and taking into consideration the natural weather conditions, the concentration value of 1.59 mg/kg As could be selected as the reference safety threshold for As in this area, in order to protect the health of personnel working in this coal mine and to ensure sustainable development of this regional environment. However, the acceptable levels of carcinogenic risk vary (the United States usually uses 10^{-6}, whereas 10^{-5} is usually used in the UK, and The Netherlands recommends a more relaxed 10^{-4} [36]), suggesting that the value of 1.59 mg/kg, calculated under a 10^{-6} acceptable carcinogenic risk level, as the safety threshold for As in the soil environment in a coal chemical industry area needs further discussion. Then, the final feasible threshold of As in the soil environment should be determined holistically by considering the background value, geological conditions, biological parameters, regional climatic characteristics and regional development planning.

4. Conclusions

Among the harmful trace elements in the Wulantuga open-cast coal mine area, the carcinogenic risk of As is most significant. High carcinogenic risk was found at a depth of 1–7 m. The highest carcinogenic risk value achieves 8.77×10^{-5}, which is 87.70-times the recommended safety value. It is necessary to adopt effective safety protection measures for personnel working in this coal mine area.

In the soil environment of the Wulantuga open-cast coal mining area, the main route of exposure of As is the inhalation of particles, which contributes to 68.64% of the carcinogenic risk. Therefore, in order to mitigate and prevent human health risk from the coal mine, blocking the inhalation particle exposure route appears to be the best method.

Considering the different control values in each exposure pathway, the minimum control value (1.59 mg/kg) in the pathway of the ingestion of soil particles can be selected as the strict reference safety threshold for As in the soil environment in the coal chemical industry area, which would provide a basis for the protection of the operators working in the area. However, the acceptable levels of carcinogenic risk vary, suggesting that the value of 1.59 mg/kg, calculated under a 10^{-6} acceptable carcinogenic risk level, as the safety threshold for As in soil environment in the coal chemical industry area needs further discussion.

Acknowledgments: The authors would like to thank the National Basic Research Program of China (973 Program, No. 2014CB238906) for financial support. We thank Shifeng Dai of China University of Mining and Technology (Beijing) for assisting in the ICP-MS analysis of heavy metals in soil samples.

Author Contributions: Jianli Jia determined the evaluation method; Ying Liu and Xiaojun Li performed the experiments; Chunyu Han and Lina Zhou analyzed the data; Peijing Wu contributed materials/analysis tools; Liu Yang provided the soil samples; Jianli Jia and Xiaojun Li wrote the paper.

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

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