GEOECOLOGY

Eco-Environmental, Human Health Risk Assessment of Soils and Crops Heavy Metals in the Typical Black-Rock Series Area in the Northern Daba Mountains, China

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Abstract—Heavy metals (HMs) pollution in the black-rock series has attracted much attention, some HMs in soils and crops exceed the safety limits. This study investigated the concentrations of heavy metals in the soil, conducting eco-environmental and human health risk assessment of heavy metals in the typical black-rock series area in the northern Daba Mountains, China. Results showed that the concentrations of As, Cd, Cr, Cu, Hg, Ni, and Zn were higher in the study area than the Chongqing soil background values. The average Cd concentration (2.40 mg/kg) was 24.7 times that of the Chinese background value. The geo-accumulation index (I_{geo}) showed that the soil was "heavily contaminated" with Cd, and uncontaminated with Pb. The potential ecological risk of heavy metals in the soil were mainly from Cd and Hg. Through a human health risk assessment based on the main crops from the study area, the exposure risk index of each heavy metal was less than 1, with Cd being the largest (0.54). However, the total index was more than 1 (1.58), indicating human health risk in the study area. Meanwhile, the exposure risk index for the potato crop was the highest among the four crops, reaching 0.69. Therefore, adjusting the planting structure in the study area, avoiding cultivating leafy vegetables with strong heavy metal absorption capacities, and reducing the potato crop sizes are all suggested measures.

INTRODUCTION

Black-rock series refer to dark gray-black siliceous rocks, carbonate rocks, argillaceous rocks, and their corresponding metamorphic rocks, with significant organic carbon and sulfide [1]. Although they are widely distributed around the world, the Yangtze River Basin in China is the largest distribution area, spanning ~1600 km from the southwest to the east coast along the Yangtze River [2, 3] These rocks are formed in reducing environments in stagnant water, and are rich in heavy metals [4–8]. They are typical natural geological background sources of heavy metals, which can be decomposed by chemical weathering in super-

gene environments [8, 9]. Previous studies have shown that the soil derived from the black-rock series is generally rich in heavy metals (with As and Cd showing the highest concentrations [10], reaching levels that can be deemed as pollution [9], thereby posing significant ecological risk. In addition, the bioavailable Cd content in this soil is higher than that from other parent-rock areas. Since Cd is easily absorbed by organisms, it can result in human health risks [5, 11]. However, there is a paucity of studies focusing on soil heavy metal distributions and ecological health risk assessments of the black-rock series.

A set of typical black-rock series from the Lower-Cambrian was discovered in the northern Daba Mountains, Chongqing, China. This region is also the production base for large-yield and good-quality potatoes and other special agricultural products in Chongqing. Potatoes have become the staple food of the locals. So far, there are relatively few studies on the HMs geochemical characteristics, eco-environmental and health risk assessment of soils and crops in the black rock series area, and whether it will cause ecological risk.

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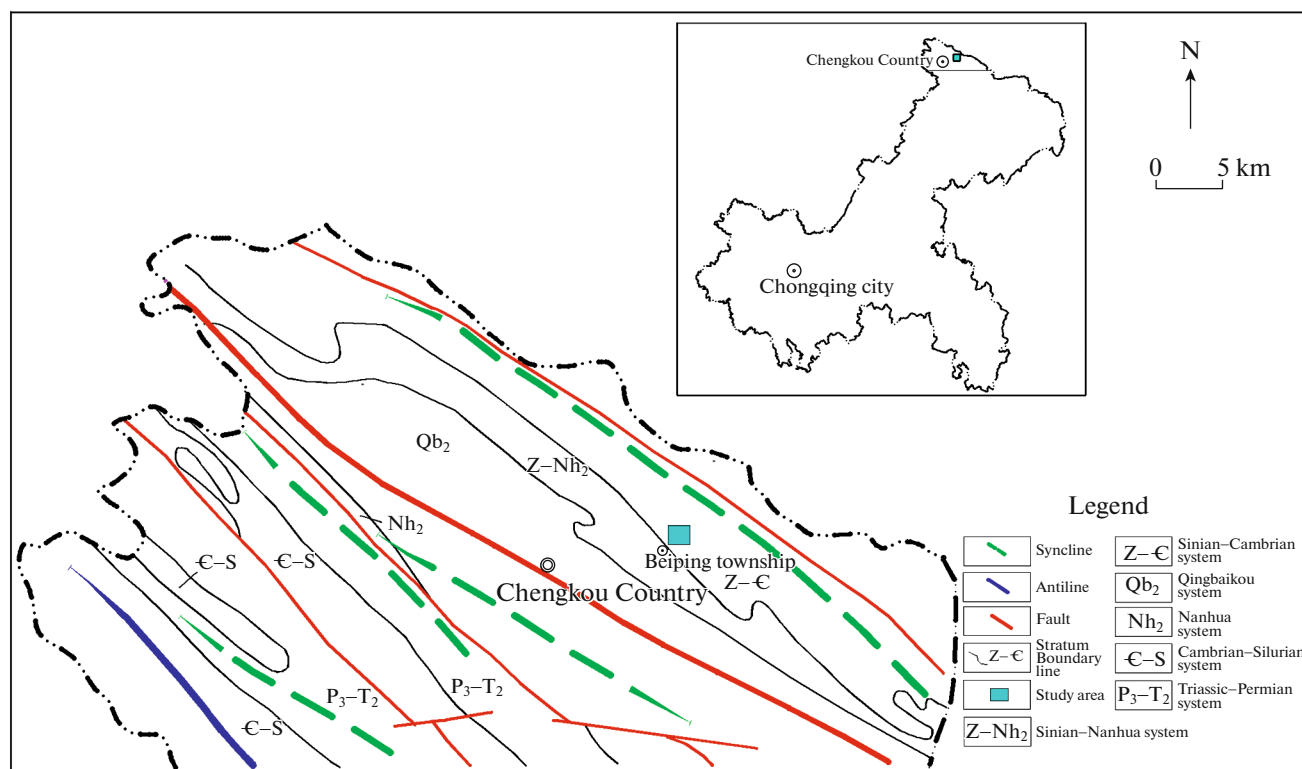
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Fig. 1. Map showing the study area.

In this study, we analyze the geochemical characteristics of heavy metals in the soil and the degree of heavy metal pollution in the LuJiaPing Formation of the North Daba Mountains, Beiping, Chongqing and assess the ecological and human health risk due to the heavy metal pollution. This study provides a scientific basis for the prevention and control of soil heavy metal pollution, ecological preservation, and health protection.

STUDY AREA

The study area is located in the north of Chengkou County in the northeastern part of Chongqing, China, at the junction between the Sichuan, Shanxi, and Chongqing provinces (see Fig. 1). It belongs to the northern subtropical mountain climate of the Sichuan Basin and the subtropical monsoon climate zone. The terrain is mainly high mountains, with an altitude of 2000−2500 m and a relative height difference of about 1000 m. Mountains and valleys alternate from the southwest to the north. The study area is located at the junction of the Qinling geosyncline and the Yangtze Platform in the hinterland of the northern Daba Mountains. It is an arc-shaped structural belt. Rock outcrops in the study area include lithologies from the NanHua to Cambrian. The black-rock series in the study area occur in the LuJiaPing Formation of the Lower-Cambrian, with gray-black carbonaceous silt-stone, carbonaceous silty slate, siliceous slate, and metasiltstone. Soils are typically yellow soil and yellow-brown soil.

MATERIALS AND METHODS. SAMPLING AND ANALYSIS

A total of 251 surface soil samples (0−20 cm depth) were collected from the LuJiaPing Formation stratum area of Beiping Township using a grid sampling design in 2018. The sampling density was ~18 samples per 1 km². At each sampling site, about 4−6 sub-samples were collected from a 30−50 m radius around the sampling point to form mixed samples with 1.0~1.5 kg. Root, straw, stones, and other debris were removed from the samples. All samples were air-dried; sieved through a 20 mm nylon sieve after clearing visible debris, pebbles, and stones; and then milled with an agate grinder until fine particles (<200 μm) were obtained for analyses. Each dried sample was stored in brown glass bottles until analysis. At the same time, 217 plant samples in the study area were collected from edible parts, including potato, sweet potato, radish, and corn, which are the main crops for the locals. The samples were washed with pure water to remove the adhered soil and pollution caused by fertilizer and pesticide spraying. Then, the samples were washed with distilled water 1−2 times and dried at an appropriate temperature range.

Soil and plant samples were analyzed in a special laboratory of the Ministry of Land and Resources of China. In addition, 30 samples of 251 soil samples were determined for the fractions of HMs based on the modified Tessier sequence extraction method [17] and the technical requirements for regional biogeochemical evaluation (DD2005-03) [31]. According to this method, a total of seven fractions of HMs could be obtained, including water-soluble, ion-exchangeable, bound to carbonates, bound to humic acid matters, bound to iron-manganese oxides, bound to strong organic matters, and residual. Different fractions of HMs had different bioavailability and toxicity to animals and plants [18]. Residual had the smallest activity, belonged to stable state and had no bioavailability, while water-soluble and ion-exchangeable were the most easily absorbed by organisms, belonged to active state and had bioavailability, and the activity of other fractions would change due to the changes of environmental conditions, such as pH, redox conditions; herein, they belonged to sub stable state and had certain bioavailability.

The analysis methods and quality control measures of all elements and indexes are complied with the technical requirements for regional biogeochemical evaluation of China Geological Survey (DD2005-03), and the qualified rate of quality reached 100%.

INDEX OF GEO-ACCUMULATION

The geo-accumulation index (I_{geo}), be computed using the following equation:

$$I_{geo} = \log_2\left(\frac{C_i}{1.5S_i}\right),$$

where I_{geo} is the index of geo-accumulation of each element, C_i is the measured concentration of each element, and S_i is the local geochemical background value of heavy metals in the soil, which is given in [12]. The constant 1.5 is adopted due to the natural fluctuation of baseline data [21]. I_{geo} can be classified into: (1) uncontaminated ($I_{geo} \leq 0$), (2) uncontaminated to moderately contaminated ($0 < I_{geo} \leq 1$), (3) moderately contaminated ($1 < I_{geo} \leq 2$), (4) moderately to heavily contaminated ($2 < I_{geo} \leq 3$), (5) heavily contaminated ($3 < I_{geo} \leq 4$), (6) heavily to extremely contaminated ($4 < I_{geo} \leq 5$), and (7) extremely contaminated ($I_{geo} > 5$).

EVALUATION OF POTENTIAL ECOLOGICAL RISK

The Hakanson risk index (*RI*) was used to assess the potential ecological risk of heavy metals. This method not only considered the content of heavy metals but also linked their toxicological effects, and has been widely used to evaluate ecological risks caused by

heavy metals in soil [13, 23]. It can be calculated using the following equations:

$$RI = \sum_{i=1}^{n} E_r^i = \sum_{i=1}^{n} (T_r^i \times C_f^i) = \sum_{i=1}^{n}\left(T_r^i \frac{C_i}{C_n^i}\right),$$

where C_i is the measured metal concentration, C_n^i refers to the background value of the heavy metal in soils of Chongqing, China, and T_r^i is the toxic response factor for a given substance, reported to be 40, 30, 10, 5, 5, 5, 2, and 1 for Hg, Cd, As, Cu, Ni, Pb, Cr, and Zn, respectively [13, 23]. E_r^i is the individual potential ecological risk factor, and *RI* is a composite index that represents the potential ecological risk of all the heavy metals in soils combined, and *n* is the total number of the determined heavy metals. E_r^i and *RI* are generally defined using five grades.

RISK ASSESSMENT BASED ON BIOLOGICAL ACTIVITY OF HEAVY METALS

Sundaray et al. [24] assessment the environmental risk of heavy metals through the risk assessment code (RAC) method. The proportion of water-soluble, ion-exchangeable, bound to carbonates of heavy metals in the soil (usually referred to as F1) was used as the bioavailable component. The assessment results were generally classified into five levels: no risk (F1 ≤ 1%), low risk (1% < F1 ≤ 10%), and medium risk (11% < F1 ≤ 30%), high risk (31% < F1 ≤ 50%), extremely high risk (F1 > 50%) (heavy metals are easy to enter the food chain).

HEALTH RISK ASSESSMENT. AVERAGE DAILY EXPOSURE OF HEAVY METALS

The average daily intake (*ADI*) of heavy metals through dietary and other environmental exposure was determined based on the methods by Y. Liu et al. [14] described by the following equation:

$$ADI = \sum \frac{C_i D_i}{BW},$$

where *ADI* is the average daily intake of heavy metals (mg/kg d); *BW* is the average body weight, which was assumed to be 60 kg for Chinese adults [15]; C_i is the concentration of each heavy metal in the food crops and other media; D_i is the daily intake of foodstuffs (kg/d). The number of heavy metals ingested through diet is much higher than that inhaled through skin contact and respiration, and the drinking water quality and air in the study area are good. Therefore, only the main staple crops in the region were evaluated in the study.

The study area is far away from the city, and the life style of its residents is relatively traditional. Potatoes, sweet potatoes, corn, and radish have become the sta-

ple food of the residents. Rice, meat, fruit, and other food are usually purchased from the market rather than produced in the study area. According to a large number of survey data, the daily consumption values of potatoes, sweet potatoes, corn, and radish were 200, 140, 140, and 50 g/d, respectively.

HUMAN HEALTH RISK ASSESSMENT

According to the USEPA method [19], the risk of non-carcinogenic effects is expressed as HQ, which is the ratio of the dose resulting from exposure to the site media compared to the highest dose without the risk of adverse effects. The HQ through dietary exposure could be assessed based on the oral reference dose (RfD) for heavy metals and was determined by the following equation:

$$HQ = \frac{ADI}{RfD}.$$

If $HQ < 1$, there is no significant risk of non-carcinogenic effects; if $HQ > 1$, there is a chance that non-carcinogenic effects may occur, with a probability which tends to increase as the HQ increases. The reference oral doses of heavy metals for adults are given in [28, 30].

RESULTS AND DISCUSSION. GEOCHEMICAL CHARACTERISTICS OF HEAVY METALS IN THE SOIL

The soil concentrations of heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn) are shown in Table 1. The average concentrations and the 95% confidence intervals of the metals were much higher than their respective background values in Chongqing, except Pb, which was slightly lower. The average concentration of Cd is 21 times higher than its background values in Chongqing and 24.7 times higher than its background values in China. The average concentrations of the other metals are 1−3 times higher than their background values in Chongqing. The ratio of heavy metal concentrations to their background values in Chongqing decreased in the following order: Cd > Zn > As > Hg > Ni > Cr > Cu > Pb. Compared to the typical black-rock series soil in the study area, the concentrations of heavy metals was significantly lower in central Hunan [9], Western Zhejiang [21], and the Okchon Zone in Korea [2], and higher in Jianping, Chongqing [11] (see Table 1).

According to previously published results, the average concentrations of heavy metals in the study area rocks are much higher than in the upper crust and world shale [10] (see Table 1), suggesting that the heavy metal geochemical background values in the study area are higher. As no industrial activities and expressways are found in the area, the heavy metal enrichment in the soil may be the result of natural bedrock weathering.

The soil pH value in the study area ranged from 4.7 to 8.3. The distribution characteristics of the heavy metals in different ranges are shown in Fig. 2. According to the Chinese Soil Environmental Quality Risk control standard (RCS) for the soil contamination of agricultural land [20], the rates of exceedance of the concentration of each element beyond the risk screening value (RSV) decreased in the following order: Cd > Zn > Ni > Cu > As > Cr > Hg > Pb, with rates of 71.21, 34.55, 26.06, 24.42, 21.52, 18.18, 3.03, and 0.3%, respectively. The results compared with RCS showed that each heavy metal in the soil had concentrations more or less beyond the RSV. Cd reached heavy metal pollution levels, and Pb remained at a safe level.

ANALYSIS OF HEAVY METAL POLLUTION IN THE SOIL

The I_{geo} of the heavy metals based on the soil background value in Chongqing is showed in Table 3. Results show that the I_{geo} of Cd is the highest, with a mean value greater than 3. Its maximum I_{geo} value is greater than 7, suggesting that Cd fell into the "heavily contaminated" category. The mean I_{geo} value for As is 1.5, suggesting that As could be classified in the "moderately contaminated" category. However, the lowest mean I_{geo} value was exhibited by Pb (it in the negative). Thus, soils in the study area were uncontaminated by Pb. The mean I_{geo} values for the other metals were between 0 and 1, suggesting that the soils in the study area were "uncontaminated to moderately contaminated." The mean I_{geo} values decreased in the following order: Cd > As > Hg > Zn > Ni > Cu > Cr > Pb.

POTENTIAL ECOLOGICAL RISK ASSESSMENT

Using the soil background value in Chongqing as a reference, the E_r values of the eight heavy metals in the study area soil are shown in Table 2. The mean E_r values of Cr, Cu, Ni, Pb, and Zn were less than 40, indicating that these metals posed a low potential ecological risk. The mean E_r value of As was 51, indicating a moderate potential ecological risk. The mean E_r value of Hg was 143, indicating a considerable ecological risk. In contrast, Cd had a higher mean E_r value (653) than the other heavy metals; 58.1% of all samples for E_r (Cd) were greater than 320, demonstrating a dangerous ecological risk level.

The RI values of the heavy metals in the study area ranged from 108 to 6810, with a low ecological risk level accounting for 3.6%, moderate ecological risk level for 17.1%, considerable ecological risk level for 27.1%, high ecological risk level for 30.7%, and very high ecological risk level for 21.5% of the samples. The mean RI value is ~880, at a high ecological risk level and mainly caused by Cd in the soil.

Table 1. Concentrations distribution of heavy metals in the study area and other typical areas

			As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Study area	Soil	Range	4.3–85.6		38–708	15.7–240.6	0.04–2.66	20–393.7	6.5–115.4	66–1252
		Mean	25.61	2.40	147.72	57.12	0.21	78.5	24.29	262.88
		95% CL[a] UB[b]	27.64	2.7688	158.63	61.58	0.25	84.63	25.2	287.2
		95% CL[a] LB[c]	23.59	2.0248	136.85	52.66	0.18	72.37	23.37	238.55
	Parent rock	Range	32.7–109.9	0.93–93.77	75–1004	58.2–450.1	–	64.6–133.1	8.6–53.6	166–1161
		Mean	78.1	23.18	586	215.7	–	90.3	35.3	639
Wushan soil [11]		Range	–	0.42–42	73–884	23–96	–	28–252	23–53	82–644
		Mean	–	7.1	301	50	–	95	36	230
Central Hunan soil [9]		Range	–	0.41–4.79	85.2–162	46.3–94.7	–	24.3–135	18.2–71.1	61.2–413
Western Zhejiang soil [21]		Range	2.09–144.08	0.07–13.03	17.9–106.7	11.1–398.1	0.04–0.49	8.7–114.4	21.6–198.5	43.6–616.6
		Mean	13.29	0.81	53.73	33.31	0.12	25.34	38.94	113.04
Okchon Zone soil [2]		Range	–	0.2–20.1	15–280	18–403	–	20–580	12–137	50–1100
		Mean	–	1.18	78.1	57.4	–	54.6	40.2	161
The soil background values in Chongqing [12]			5.000	0.110	80.000	26.000	0.060	32.000	26.000	80.000
The soil background values in China [22]			11.200	0.097	61.000	22.600	0.065	26.900	26.000	74.200
The risk screening value of agricultural land soil pollution in China [20]		pH ≤ 5.5	30	0.3	150	50	0.5	60	70	200
		5.5–6.5	30	0.3	150	50	0.5	70	90	200
		6.5–7.5	25	0.3	200	100	0.6	100	120	250
		pH > 7.5	20	0.6	250	100	1	190	170	300
World shale [10]		Mean	13	0.3	90	45	0.18	68	31	95
Upper crust [10]		Mean	4.8	0.09	92	28	0.05	47	17	67

[a] The 95% Confidence Interval for Mean, [b] means the Upper Bound, [c] means the Lower Bound.

Table 2. The classification of heavy metals in soil based on the I_{geo}, and potential ecological risk coefficient in the soil

	Heavy metal	Min.	Max.	Mean	uncontaminated	uncontaminated to moderately contaminated	moderately contaminated	moderately to heavily contaminated	heavily contaminated	heavily to extremely contaminated	extremely contaminated
								Sample numbers			
I_{geo}	As	−0.81	3.51	1.50	11	66	103	64	7	0	0
	Cd	0.11	7.14	3.14	0	21	39	54	65	51	21
	Cr	−1.67	2.56	0.12	120	99	31	1	0	0	0
	Cu	−1.31	2.63	0.33	85	121	38	7	0	0	0
	Hg	−1.34	4.88	0.88	39	109	79	19	2	3	0
	Ni	−1.26	3.04	0.48	76	111	59	4	1	0	0
	Pb	−2.59	1.57	−0.73	250	0	1	0	0	0	0
	Zn	−0.86	3.38	0.83	56	95	70	26	4	0	0

		Min.	Max.	Mean	low potential ecological risk	moderate potential ecological risk	considerable ecological risk	high ecological risk	dangerous ecological risk
					Sample numbers				
E_r	As	8.54	171.30	51.22	120	81	48	2	0
	Cd	48.45	6330.21	653.70	0	16	34	55	146
	Cr	0.94	17.70	3.69	251	0	0	0	0
	Cu	3.02	46.27	10.98	249	2	0	0	0
	Hg	23.75	1772.54	143.06	7	63	120	48	13
	Ni	3.13	61.51	12.27	249	2	0	0	0
	Pb	1.24	22.19	4.67	251	0	0	0	0
	Zn	0.83	15.65	3.29	251	0	0	0	0
RI		108.82	6810.68	882.88	9	43	68	77	54

RISK ASSESSMENT BASED ON BIOLOGICAL ACTIVITY OF HEAVY METALS

The total heavy metal concentrations in the soil of the study area are high, especially for Cd, causing potential harm to the ecological environment. However, the mobility and bioavailability of heavy metals largely depend on their chemical form and speciation in the soil. Different chemical forms and speciation produce different environmental effects, directly affecting the toxicity, migration, and circulation of heavy metals in the soil. The ion-exchangeable and bound to carbonates are often considered as bioavailability fraction together with the water-soluble (F1). Bound to humic acid matters (F2), bound to iron-manganese oxides (F3) and bound to strong organic matters (F4) are considered as potential bioavailable components, which can be used by plants in strong acid medium. Residual (F5), also known as stable state, exists in the mineral lattice, which is difficult to release and cannot be used by plants [25].

The partitioning of sequentially-extracted element concentrations in the soil is shown in Table 3. The results show that the speciation percentage of Cd in soil was F1 > (F2 + F3 + F4) > F5, while the other

Table 3. Fractions of heavy metals in the soil of the study area

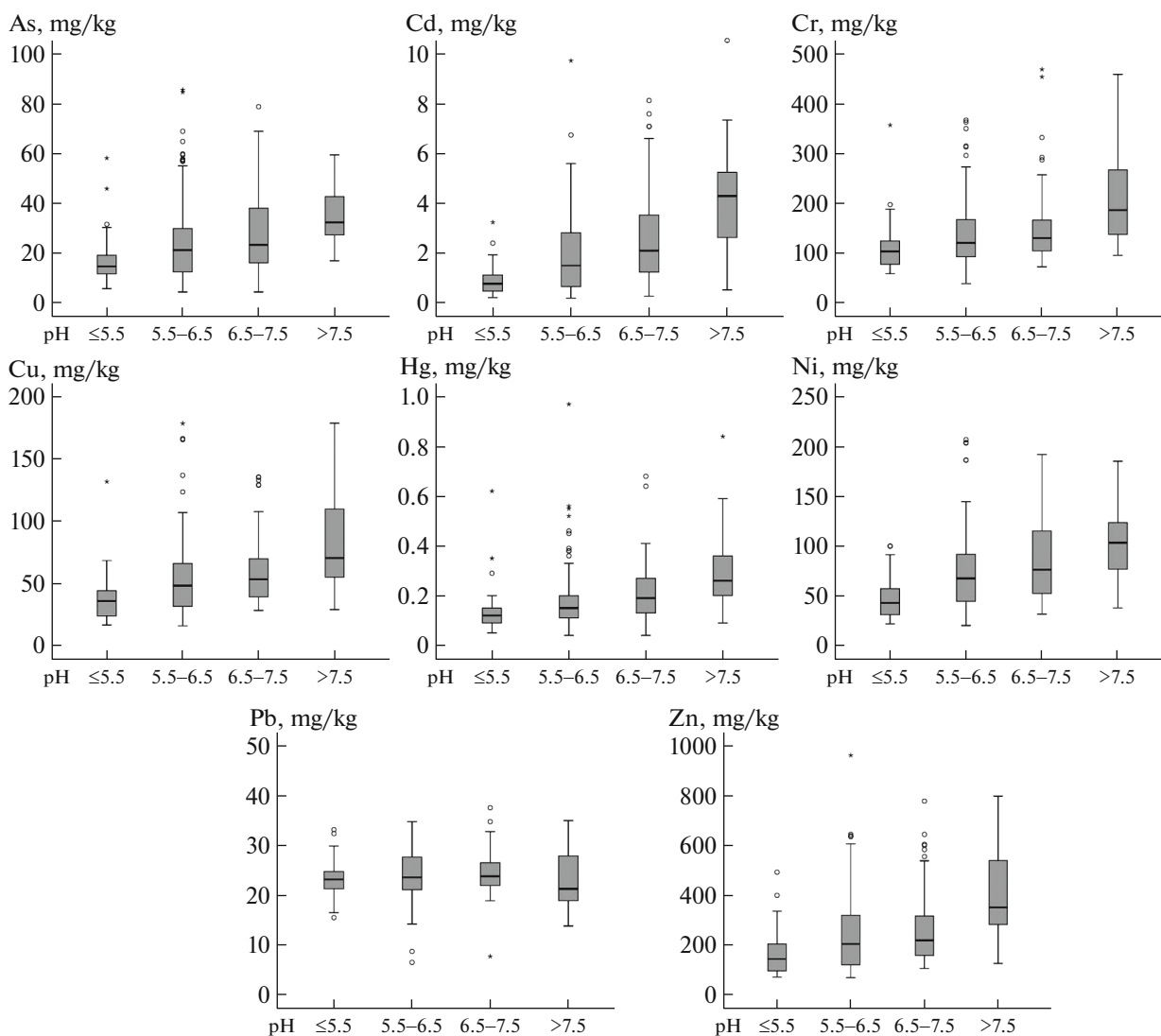| Heavy metal	Bioavailability fraction ($n = 30$), %				
	F_1	F_2	F_3	F_4	F_5
As	1.69	15.08	8.48	0.23	74.52
Cd	46.04	17.37	11.04	5.23	20.38
Cr	1.55	3.68	1.30	3.52	89.94
Ni	3.13	5.48	9.27	6.85	75.26
Cu	2.25	23.51	10.55	3.22	60.46
Hg	3.60	17.99	0.90	14.98	62.53
Pb	4.28	8.21	29.78	0.62	57.10
Zn	2.34	4.65	7.14	6.27	79.60

Fig. 2. Box-plots of heavy metals concentrations in the study area.

seven heavy metals were F5 > (F2 + F3 + F4) > F1. Cr (89.94%), Zn (79.6%), Ni (75.26%), As (74.54%), Hg (62.53%), Cu (60.46%), and Pb (57.1%) are mainly present as residual fractions. The bioavailability fraction (F1) percentages decreased in the following order: Cd (46.04%) > Pb (4.28%) > Hg (3.6%) > Ni (3.13%) > Zn (2.34%) > Cu (2.25%) > As (1.69%) > Cr (1.55%). It means that Cr, Pb, Ni, Hg, Zn, As, and Cu are at low risk, while Cd is at high risk.

GEOCHEMICAL CHARACTERISTICS OF HEAVY METALS IN CROPS

Except Ni was not detected because it was lower than the detection limit, the concentrations of other 7 heavy metals in the potato, sweet potato, corn, and radish crops are shown in Table 4. Compared to the national food safety standard pollutant limits in food

[27], the average concentrations of heavy metals in the four crops were within the safe range. However, the Cd concentrations in the four crops exceeded the standard. Hg concentrations only exceeded the standard in potatoes, with a rate of exceedance beyond the standard of 6.25%. The other heavy metals did not exceed the standard in any of the crops.

The high Cd concentrations in some samples of the four crops may be related to the high proportion of bioavailable forms of Cd in the soil in the study area, allowing it to migrate more easily to the crops than the other heavy metals. The ability of the crops to absorb heavy metals is not only related to the forms of heavy metals in the soil, but also the crop types. The Cd content in different crops in black shales and slates of the Okchon Zone, Korea is as follows: Chinese cabbage > red pepper > soybean = sesame > rice stalk > corn > rice grain [5]. The Cd content in different crops in the

Table 4. Concentrations of heavy metals in the plant in the study area (mg/kg)

Crops	Concentrations	As	Cd	Cr	Cu	Hg	Pb	Zn	Ni
Potato (n = 48)	Min.	0.0050	0.0150	0.0330	0.0040	0.0007	0.0500	2.4400	Not detected
	Max.	0.0310	0.1480	0.0990	2.2200	0.1940	0.0500	8.4300	
	Mean	0.0128	0.0672	0.0614	1.2725	0.0058	0.0500	4.1531	
	Over standard rate%	0	12.5	0	–	6.25	0	–	
Sweet potato (n = 42)	Min.	0.0050	0.0150	0.0378	0.5005	0.0007	0.0500	1.0500	Not detected
	Max.	0.0328	0.2396	0.2368	1.3473	0.0007	0.0500	9.0872	
	Mean	0.0062	0.0452	0.0784	0.9257	0.0007	0.0500	1.8434	
	Over standard rate%	0	4.76	0	–	0	0	–	
Corn (n = 80)	Min.	0.0103	0.0150	0.0943	0.4920	0.0007	0.0500	5.5740	Not detected
	Max.	0.0186	0.8340	0.9400	2.9500	0.0025	0.1368	30.2500	
	Mean	0.0132	0.0661	0.1947	1.2479	0.0009	0.0534	13.9368	
	Over standard rate%	0	11.25	0	–	0	0	–	
Radish (n = 48)	Min.	0.0050	0.0150	0.0341	0.1476	0.0007	0.0500	1.1400	Not detected
	Max.	0.0194	0.2800	0.2074	0.4200	0.0007	0.0500	9.0990	
	Mean	0.0082	0.0668	0.0733	0.2558	0.0007	0.0500	2.6397	
	Over standard rate%	0	19.15	0	–	0	0	–	

n means the number of samples, '–' means that the element limit in crops is not determined in National food safety standard pollutant limit in food.

Table 5. The average daily exposure of the seven heavy metals (μg/d)

Crop	As	Cd	Cr	Cu	Hg	Pb	Zn
Potato	2.56	13.44	12.28	254.49	1.16	10.00	830.63
Radish	1.15	9.35	10.26	35.82	0.10	7.00	369.56
Sweet potato	0.87	6.32	10.98	129.60	0.10	7.00	258.07
Corn	0.66	3.31	9.74	62.39	0.04	2.67	696.84
Total	5.24	32.41	43.26	482.30	1.41	26.67	2155.09

Jianping black-rock soil region of Wushan, China also shows a similar trend. The Cd content in leafy vegetables is higher than that in other vegetables. However, it was found that while some of the crop samples exceeded the standard, their mean value was within the safe range, and the exceedance rate was not high. This may be due to a relatively weak absorption capacity of the local crops such as potatoes, sweet potatoes, and corn.

HUMAN HEALTH RISK ASSESSMENT BASED ON CROPS. ANALYSIS OF DAILY AVERAGE EXPOSURE OF HEAVY METALS

The average daily exposure of the seven heavy metals is shown in Table 5. The daily average exposure of each heavy metal ingested via the four crops, from the highest to lowest is Zn > Cu > Cr > Cd > Pb > As > Hg. In addition, the average daily exposure of potatoes was higher than that of other crops, while the average daily exposure of corn to As, Cd, Cr, Hg, and Pb was the lowest, given the dietary habits of the locals.

HUMAN HEALTH RISK ASSESSMENT

According to the statistics, for the long-term intake of the above four crops for adults, the exposure risk indexes (HQ) of the seven heavy metals decreased in the following order: Cd (0.54) > As (0.29) > Cr (0.24) > Cu (0.20) > Zn (0.12) > Pb (0.11) > Hg (0.08). The single element HQ was not more than 1 (see Fig. 3), indicating that the single element human health risk in the study area is low. However, the total HQ of the seven heavy metals was 1.58, indicating a human health risk. Among them, HQ of Cd was the largest and closest to 1, accounting for 34.2% of the seven heavy metals.

The Cd content in the study area soil and the proportion of its bioavailable form are relatively high. However, potatoes and other crops are mainly planted in the area, and the ability of these crops to absorb Cd is weaker than leafy vegetables. Therefore, human
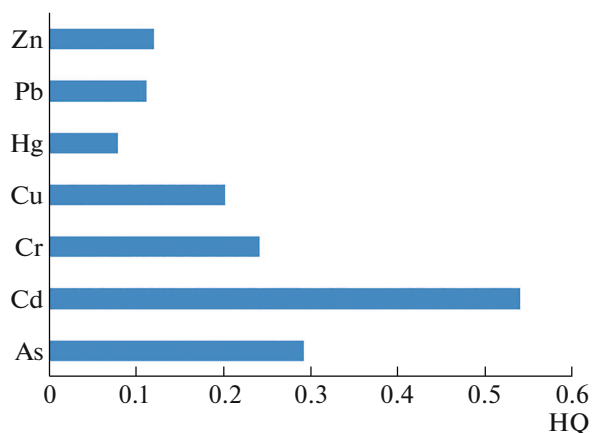
Fig. 3. The HQ of each heavy metal element.

Fig. 4. Total HQ of seven heavy metal elements in the four crops.

health risks caused by eating local crops in the study area are within the safe range. The total *HQ* of the four crops decreased in the following order (see Fig. 4): potato (0.69) > radish (0.35) > sweet potato (0.32) > corn (0.22). This is likely because the consumption of soil beans was the largest in the region, and the exceedance rate of the concentration of Cd beyond the RSV was also higher than that of other crops.

The health risk caused by Cd in the Jianping black-rock series area of Wushan is far greater than that of this study area, with the total *HQ* reaching 4.33 [14], which is far higher than the safety threshold. For example, rice and vegetables are the main dietary staples of the locals in the Jianping black-rock area of Wushan. Moreover, as the Cd content in leafy vegetables is higher than the safety threshold, the Cd exposure to the locals exceeds the safety threshold. In contrast, potatoes, radishes, sweet potatoes, and corn are the main dietary staples of the locals in this study area. The metal element absorptive capacity of these crops is weaker than that of leafy vegetables, making the human health risk in this area much lower than that of Jianping. Therefore, adjusting the planting structure in the study area, avoiding leafy vegetable crops with a strong heavy metal absorption capacity, and reducing the planting scale of potatoes can reduce the health risks in this area.

CONCLUSIONS

In the study, the contents of 8 heavy metals in typical black-rock series in the northern Daba Mountains, China, were measured, and the geo-accumulation index, risk assessment based on biological activity of heavy metals, the potential ecological and health risk were evaluated. According to Chinese national standard GB 15618-2018, 71.21% Cd of the soil samples were under Cd contamination, while the rates of contamination for the rest 7 HMs are under 34.55%. Risk assessment based on biological activity of heavy
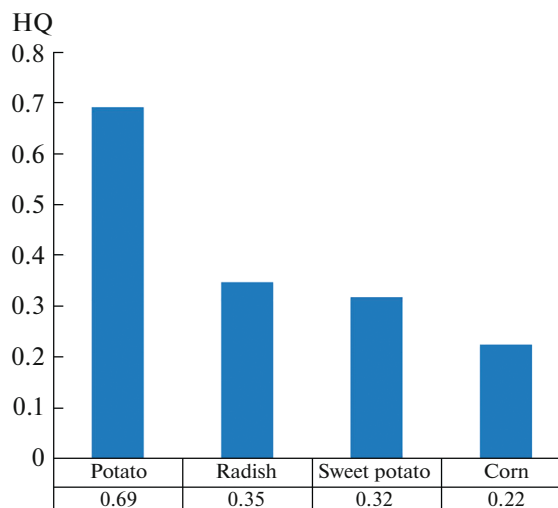
metals found that Cd was at high risk, and the geo-accumulation index showed that Cd was heavily contaminated. The potential ecological risk index RI value (882.88) indicated that the HMs in the black-rock series soil were in high ecological risk, and the contribution rate of Cd to RI was maximum (74%), which was in a dangerous ecological risk level.

The Cd concentrations in the four crops exceeded the standard, because of the high proportion of bio-available forms of Cd in the soil in the study area. According to the human health heavy metal risk assessment, the exposure risk index of a single heavy metal for the four local crops consumed by adults over an extended period is not more than 1, indicating a very low human health risk. However, the total exposure risk index of the seven heavy metals is 1.58, indicating a human health risk. Among them, the Cd exposure risk index is the largest, accounting for 34.2% of the seven heavy metal elements. In addition, potato is the most exposed among the four crops, with an exposure risk index of 0.69. Adjusting the planting structure in the study area, avoiding leafy vegetable crops with strong heavy metal absorption capacities, and reducing the planting scale of potatoes are all suggested as risk mitigating strategies.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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