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Spatial Contamination and Potential Ecological Risk Assessment of Heavy Metals in Farmland Soil around Nonferrous Metal Smeltery in North China

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Abstract: Nonferrous metallurgy is an important source of heavy metal in the environment and consequently poses potential risks to ecosystems. The impact of smelting on the surrounding environment is a concern. In this work, the content levels of selected heavy metals—chromium (Cr), nickel (Ni), copper (Cu), zinc (Zn), lead (Pb), cadmium (Cd), and arsenic (As)—were investigated separately in soil samples collected around two nonferrous metal smelteries using inductively coupled plasma mass spectrometry (ICP-MS). The spatial distribution characteristics of soil metal pollutants was studied by ArcGIS methods and the potential ecological risks were assessed by the Hakanson potential eco-logical hazard index. The results show that soils were heavily polluted by Cr, Ni, Cu, Zn, Cd, Pb, and As. Their mean contents in soil around Smeltery A were 88, 62, 103, 1200, 1.4, 146, and 69 mg/kg, respectively, and those around Smeltery B were 86, 59, 83, 117, 0.53, 57, and 65 mg/kg, respectively. Their contents were obviously higher than the background values of soil Cr (68 mg/kg), Ni (31 mg/kg), Cu (22 mg/kg), Zn (78 mg/kg), Cd (0.09 mg/kg), Pb (22 mg/kg), and As (14 mg/kg). The distribution pattern in soil and risk assessment results show that the pollution surrounding the two smelteries reached intense and moderate ecological hazard and that the contribution of Cd and As was up to 87.05% and 82.59%, respectively. These results suggest that metal smelting makes a considerable contribution to soil pollution.

Keywords: metal smeltery; soil pollution; spatial distribution; risk assessment

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1. Introduction

Soil pollution by heavy metals has been considered one of the main environmental problems due to their toxicity and persistence, and their harmful effects on the environment. Studies have shown that about one-sixth of China's agricultural soil has been subjected to different degrees of pollution by heavy metals [1]. Wang et al. [2] used principal component analysis and correlation analysis to analyze the impact of China's industrialization and urbanization on soil environmental quality. The result showed that Cr, Cu, Zn, and As were affected by natural and manmade sources, while Cd and Pb were mainly affected by manmade sources. Hg mainly comes from industrial activities, such as petrochemical production. In recent years, with increasing awareness of the hazards of heavy metals, metal smelting has become a focus of attention. Pollution from smelting is mainly discharged into the surrounding environment through the atmosphere, wastewater, and slag [3].

Ecotoxic metals are released into the environment mainly from leaky places, such as the chimneys and waste dumps of smelteries [4], and can be transferred directly to water, soil, and plants, and then eventually ingested by humans through the food chain, posing a threat to human health. Van Pelt et al. [5] investigated smelteries in the USA constructed in 1887 and found that the operation of more than 100 metal smelteries mainly involved

chimney emissions containing heavy metal particles falling to the ground, damaging the environment. Nickel et al. reported that atmospheric deposition has been identified as the main factor determining spatial variations in cadmium (Cd) and lead (Pb) contents in European mosses [6]. The continued accumulation of potentially toxic elements due to industrial pollution and overuse of agricultural chemicals severely threatens the quality of arable land [7]. Heavy metals have generally high toxicity with low content thresholds, long residence times, and persistent bioavailability [8]. They can be hazardous to human health and ecosystems at a trace level due to their ubiquity, toxicity, and persistence [9].

Nonferrous metals usually refer to all metals except iron (and sometimes manganese and chromium) and iron-based alloys. The nonferrous metal smelting process is usually considered to be one of the most important anthropogenic sources of heavy metal emissions, so smelting is raising significant concern due to the emission of toxic metals into environment, which degrades environmental quality, consequently posing a high risk to human health [10]. Li et al. [11] found that the Cd, Cu, and Pb content in soil increased closer to the smelter. Similarly, for people living near a smeltery, the absorption of toxic metals in the body increases when eating metal-contaminated wheat the closer they are to the smeltery. Hu et al. [12] conducted a follow-up survey of residents living near China's largest copper smeltery, and found that the contents of Cu and Pb in the hair, urine, and practical food of those who lived there for a long time were higher than the contents in other Chinese residents, and especially the intake of children was higher than that of adults. However, little information is available regarding the systematic assessment of spatial distribution, source apportionment, and potential ecological risk in farmland soil within the affected areas.

Topsoil is the most delicate component of environmental systems, being highly affected by smelter emissions. In order to increase the understanding of the overall environmental accumulation of heavy metals within close proximity to nonferrous metal smelting facilities, we conducted a sampling study and evaluation of the topsoil of two smelteries, and analyzed the migration and diffusion rules of toxic elements. The aims were to (1) investigate the contents and show the spatial distribution patterns of Cr, Ni, Cu, Zn, Cd, Pb, and As in soils around nonferrous metal smelteries; (2) identify the homology of soil heavy metals by principal component analysis, correlations analysis, and GIS mapping; and (3) assess the ecological risks based on the Hakanson potential ecological hazard index. The results provide insights into the management of heavy metal pollution, and this study also serves as a scientific reference for other regions both in China and worldwide.

2. Materials and Methods

2.1. Sample Collection and Preparation

Two smelteries (Smeltery A and Smeltery B) were selected to sample the topsoil of the surrounding farmland, on which mainly wheat and corn are grown. Only a small number of people live near Smeltery A, and there is no village within 2 km of Smeltery B. The sampling points were arranged about every 500 m from each smeltery to the east, west, north, and south. Taking each sampling point as the midpoint of a diagonal, 4 points on the diagonal at a distance of 1 m from the center sample point were selected as the sampling points. Five soil subsamples of about 1 kg were collected from the upper 20 cm layer around each sampling point. The five subsamples were mixed together on site. The samples were divided into 4 parts, then 1 kg of soil was selected by the quartering method. The actual sampling points are shown in Figure 1.

After taking the samples back to the laboratory, they were naturally air-dried in the shade, sieved through 20 and 100 mesh nylon net, placed in self-sealing bags, and kept for analysis.

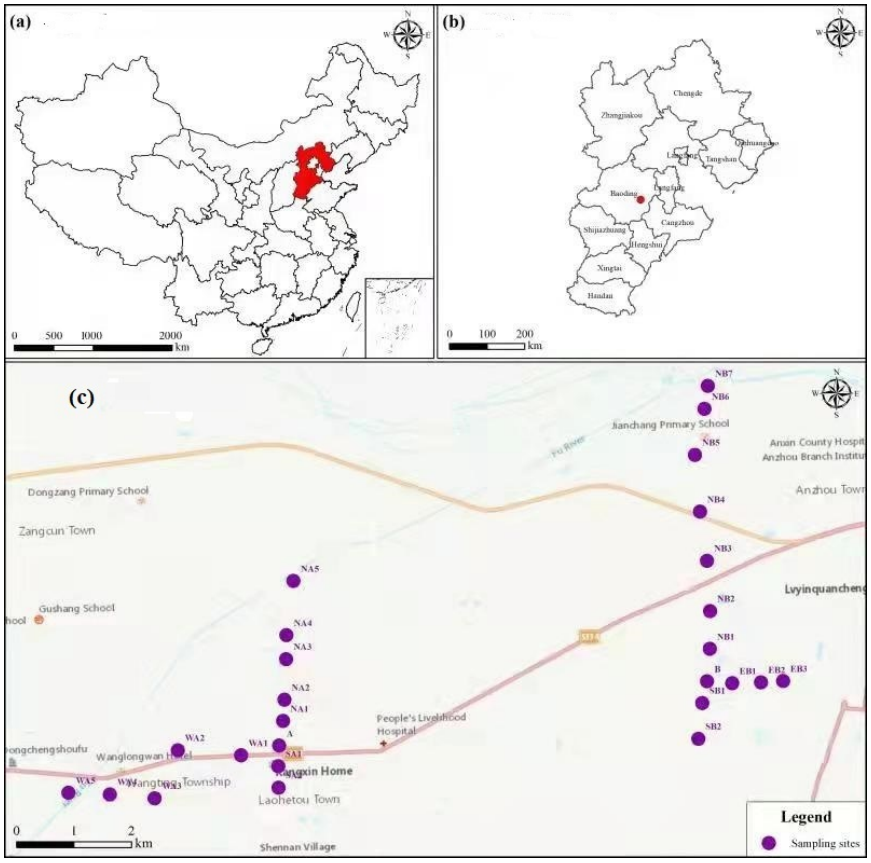

Figure 1. Sampling point location and distribution map. (**a**) Map of China; (**b**) Location map of Hebei Province in China and sampling site; (**c**) Distribution map of sampling sites.

2.2. Analysis of Heavy Metals and Quality Control

For the analysis, 0.5 g soil samples were weighed for digestion in polytetrafluoroethylene (PTFE) tubes. Then, 6 mL of nitric acid, 2 mL of hydrogen peroxide, and 2 mL of hydrofluoric acid were added and pre-digestion was carried out at room temperature for 12 h. The samples were put into the digestion furnace and dissolved at 170 °C until the liquid in the tube was evaporated to near 1 mL. After cooling, nitric acid, hydrogen peroxide, and hydrofluoric acid were again added in the same amounts as the pre-digestion step to circulate the liquid in the tube and make it clear without residue, and then the digestion solution was transferred to a volumetric flask at a constant volume.

The content of 7 toxic elements (Cr, Ni, Cu, Zn, Pb, Cd, As) was measured by inductively coupled plasma mass spectrometry (ICP-MS; XSERIES2, Thermo Fisher Scientific, Waltham, MA, USA). The ICP-MS running parameters were as follows: atomizing gas flow rate of 0.78 L/min, auxiliary gas flow rate of 0.70 L/min, ICP PF power of 1400 W, and dwell time of 40 s.

During the test, samples were maintained at a constant volume and diluted with deionized water. All glassware involved in the experiment was immersed in 5% nitric acid solution for 12 h, and then washed with tap water and deionized water. A parallel test and a national standard soil sample recovery test were used for quality control. Each test was conducted in triplicate. The sample recovery ranged from 90.67 to 100.02%.

2.3. Spatial Distribution

There was large difference in the contents of the 7 heavy metals. To intuitively display the spatial distribution of soil pollutant contents, a distribution diagram of each element was drawn [13]. ArcGIS 10.2 (v10.5, Esri, West Redlands, CA, USA) was used to provide the distribution of sampling sites [14].

2.4. Statistical Analysis

The basic statistics of the obtained data were performed with Excel 2016 (MS Office, Microsoft, Redmond, WA, USA). In order to analyze the relationships and sources of the toxic elements, SPSS Statistics 20.0 was used to conduct correlation analysis and principal component analysis of Cr, Ni, Cu, Zn, Pb, Cd, and As. Principal component analysis is a data reduction technique that reduces the number of variables to a few unrelated components and analyzes the relationships between them [15].

2.5. Risk Assessment

The Hakanson potential ecological hazard index was used to evaluate the risk of the 7 heavy metals in cultivated soil [16]. Based on the background value of heavy metals in soil, the potential ecological risk coefficient is calculated by combining the biological toxicity (toxicity response factor), environmental effect (pollution index), and environmental sensitivity to heavy metal pollution. The classification of ecological risk grade is shown in Table 1 [16,17], and the evaluation formula is as follows:

$$E_r^i = T_r^i \frac{C_i}{S_i} \quad (1)$$

$$\mathrm{RI} = \sum_{i=1}^{i} T_r^i \frac{C_i}{S_i} \quad (2)$$

where E_r^i is the ecological response coefficient of heavy metal i; T_r^i is the toxicity response coefficient of heavy metal i, with values for Cr, Ni, Cu, Zn, Cd, Pb, and As of 2, 5, 5, 1, 30, 5, and 10, respectively; E_r^i is the ecological response coefficient of heavy metal i; C_i is the measured content of heavy metal i in the sample (mg/kg); S_i is the corresponding background value (mg/kg); and RI is the comprehensive potential ecological risk index of various heavy metal elements.

Table 1. Classification of the potential ecological risk index.

Potential Ecological Risk of Single Metal (E_r^i)		Comprehensive Potential Ecological Risk Index (RI)	
Threshold Range	**Assessment Criterion**	**Threshold Range**	**Assessment Criterion**
$E_r^i < 40$	Low	RI < 150	Low
$40 \leq E_r^i < 80$	Moderate	$150 \leq$ RI < 300	Moderate
$80 \leq E_r^i < 160$	Considerable	$300 \leq$ RI < 600	High
$160 \leq E_r^i < 320$	High	RI $\geq$ 600	Very high
$E_r^i \geq 320$	Very high		

3. Results and Discussion

3.1. Contents Analysis of Seven Toxic Elements in the Soil

The contents of seven toxic elements in soil samples from around the two smelteries were determined by ICP-MS, and the results are listed in Table 2. The average contents of the seven metals are shown in Figure 2.

Table 2. Contents of seven toxic elements in tested soil samples.

Smeltery	Content	Cr	Ni	Cu	Zn	Cd	Pb	As
Smeltery A	Maximum (mg/kg)	117	86	156	391	3	503	96
	Minimum (mg/kg)	68	46	64	98	0.49	45	49
	Average content (mg/kg)	88	62	103	200	1.4	146	69
	Standard deviation	15	11	29	77	0.60	131	15
	Coefficient of variation (%)	15.4	15.83	24.09	25.58	34.26	76.58	20.89

Table 2. *Cont.*

Smeltery	Content	Cr	Ni	Cu	Zn	Cd	Pb	As
Smeltery B	Maximum (mg/kg)	127	87	190	273	1.3	287	101
	Minimum (mg/kg)	63	40	33	65	0.26	27	40
	Average content (mg/kg)	86	59	83	117	0.53	57	65
	Standard deviation	18	15	38	60	0.23	60	16
	Coefficient of variation (%)	21.15	25.83	46.09	50.78	43.87	105.3	24.33
Soil background value (mg/kg) [18,19]		68	31	22	78	0.09	22	14
Standard limit (mg/kg) [20]		250	190	100	300	0.6	170	25

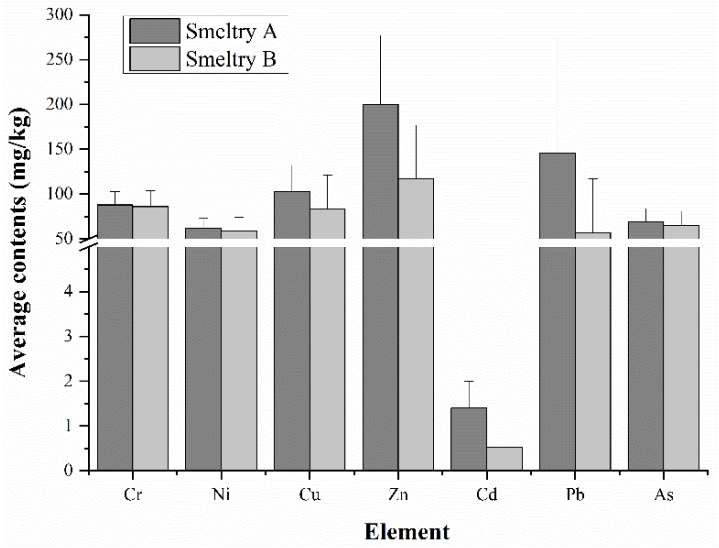

Figure 2. Average contents of heavy metals in soil near two smelters.

The average contents of all seven toxic elements around the two smelteries exceeded the local soil background values [18,19]. The detected contents of Cu, Cd, Pb, and As in farmland soil near Smeltery A were 4.68, 15.56, 6.64, and 4.93 times the background content, respectively. The contents of Cu, Cd, and As in the soil near Smeltery B were 3.77, 5.89, and 4.64 times the background content, respectively. Cd was the most serious metal around the two smelteries that exceeded the background value. Pollution by these heavy metals was mainly caused by the large amount of industrial dust produced during the process of heavy metal smelting and soil pollution caused by long-term atmospheric particulate matter deposition [21]. Compared with the risk control standard for the soil contamination of agricultural land promulgated in 2018 [20], Cu, Cd, and As in soil around Smeltery A and As in soil near Smeltery B exceeded the risk screening value of soil pollution on agricultural land. The contents of other elements did not exceed the standard limits. These results indicate that there may be risks when land is used for agriculture, and safety measures, such as agronomic regulations, should be implemented.

The coefficient of variation can be used to reflect the average variation of each sampling point [22]. From Table 2, Pb was the toxic element with the largest coefficient of variation (CV) in both Smeltery A and B. A CV greater than 50% indicated that there were pollution sources or foreign pollutants near the sampling point [23]. Besides Pb (76.58%), the CV of the six other toxic elements in the vicinity of Smeltery A were all between 15 and 35%, with a moderate degree of variation. From Figure 2, the variation degree of Cu, Zn, and Cd around Smeltery B was relatively large, indicating that the heavy metal data near the two smelteries have certain variability and an uneven distribution.

3.2. Spatial Distribution of Seven Toxic Elements

The analysis of the spatial distribution of the seven heavy metals is helpful to identify areas with high concentrations and evaluate the main sources of heavy metals [24]. The distribution of the seven heavy metals around Smeltery A and B are shown in Figure 3.

Around Smeltery A, the highest contents of Cr, Ni, Cu, Pb, Cd, As, and Zn were within 1 km to the east or north, with values up to 117, 86, 156, 503, 96, and 391 mg/kg, respectively. Smeltery A was about 5 km west of Smeltery B. The superposition of heavy metals discharged by the two smelteries led to higher contents 2–3 km west of Smeltery A. Northwest wind prevails in the study area in winter and southeast wind prevails in summer. Therefore, on the whole, the content of heavy metals in the north–south direction is higher than that in the east–west direction. During the sampling survey, it was found that there was an abandoned metal recycling smeltery about 0.5 to 1 km southwest of Smeltery A, which was a possible cause of the increased Zn and Cd contents in the soil southwest of Smeltery A. As for Smeltery B, there were several small waste and lead battery recovery plants in the vicinity, which had a great influence on the distribution of heavy metals, resulting in an irregular distribution of heavy metals, as shown in the distribution diagram. Therefore, it was necessary to analyze the relationship between the contents of the seven heavy metals and Smeltery B through correlation analysis and principal component analysis.

3.3. Homology and Principal Component Analysis of Heavy Metals in Soil

The correlation between elements indicated that elements generally had homology or compound contamination. Pearson correlation coefficient analysis and principal component analysis (PCA) were used to analyze the relationship between heavy metal elements in soil and their possible sources. Correlation analysis of heavy metals is listed in Table 3.

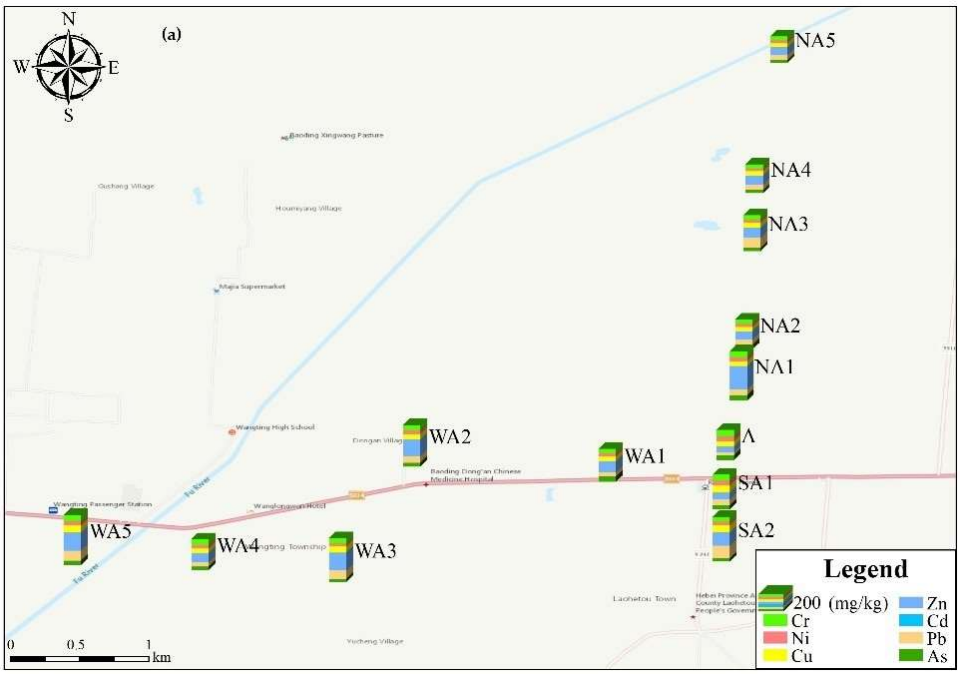

Figure 3. *Cont.*

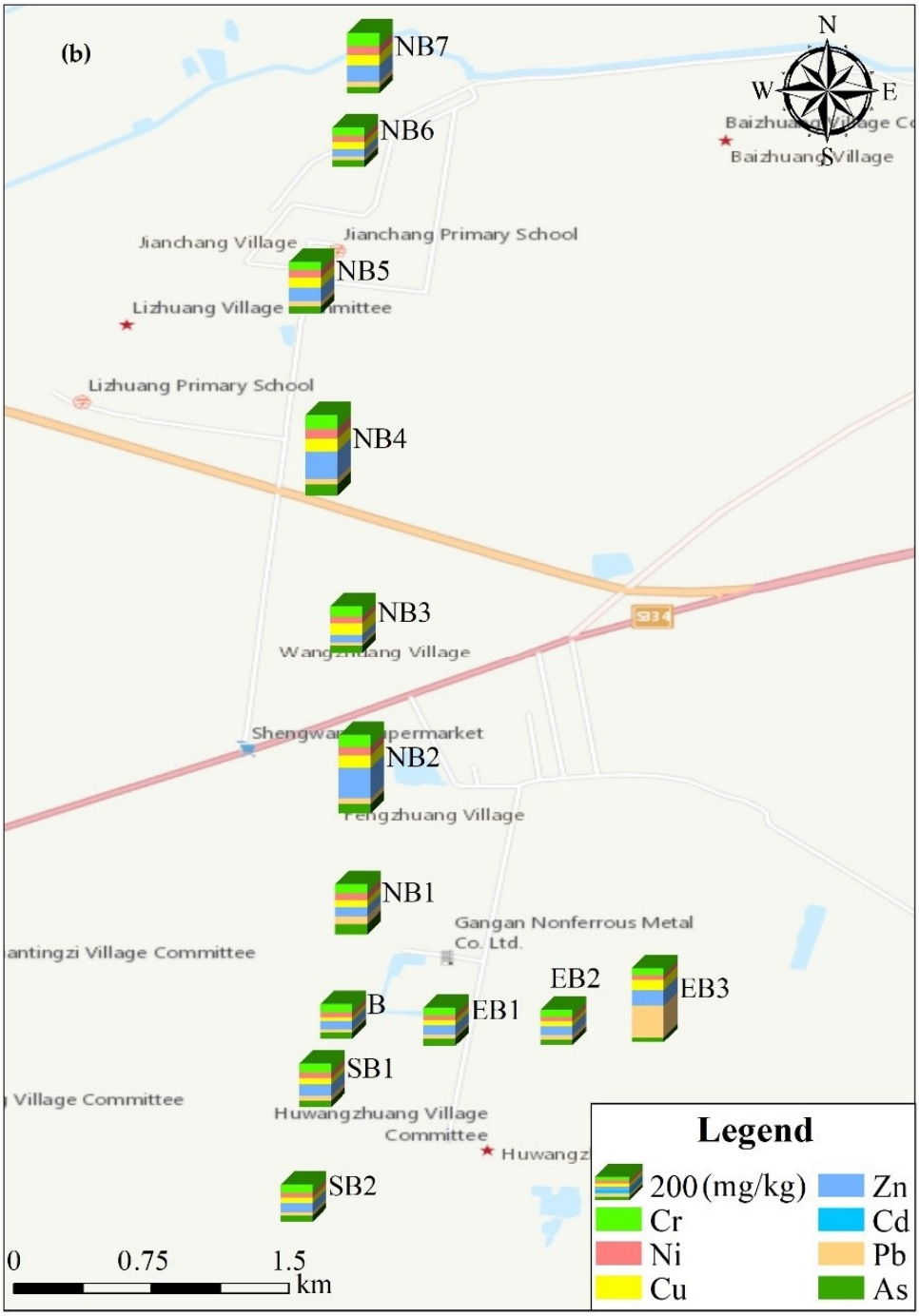

Figure 3. Spatial distribution of heavy metals in soil surrounding Smeltery A and B. (**a**) Smeltery A; (**b**) Smeltery A and B.

The results in Table 3 show that there was a certain interrelation between Cr, Ni, Cu, Pb, and As in the soil of the two smelteries. From the correlation analysis, the correlation coefficient of Cr, Ni, and As in the soil near Smeltery A was 0.565 and 0.407, respectively, indicating a moderately positive correlation between these three metals. The correlation coefficient of Ni, Cu, and As was 0.648 and 0.629, respectively, indicating a strong positive correlation between these three metals. The correlation coefficient between Ni and Pb was 0.498, indicating that Ni and Pb have a moderately positive correlation. According to the correlation coefficient, Cu has a moderately positive correlation with Cd and Pb, Zn and Cd have a moderately positive correlation, and Cd and Pb have a very strong positive correlation. The correlation coefficient of Cr and Ni, Zn, and As in the soil near Smeltery B

was 0.773, 0.610, and 0.632, indicating a strong positive correlation between Cr and Ni, Zn, and As, and between Ni and Cu, Zn, and As. There is a strong positive correlation between Cu and Zn, and between Zn and As. There is a moderate positive correlation between Zn and As, and a very strong positive correlation between Cd and Pb.

Table 3. Correlation analysis of heavy metals in soil near Smeltery A and B.

Smeltery		Cr	Ni	Cu	Zn	Cd	Pb	As
Smeltery A	Cr	1						
	Ni	0.565 *	1					
	Cu	0.312	0.648 **	1				
	Zn	0.122	0.100	0.188	1			
	Cd	−0.248	0.210	0.556 *	0.459	1		
	Pb	0.053	0.498 *	0.545 *	0.189	0.679 **	1	
	As	0.407	0.629 **	0.190	0.179	−0.047	0.217	1
Smeltery B	Cr	1						
	Ni	0.773 **	1					
	Cu	0.344	0.707 **	1				
	Zn	0.610 **	0.658 **	0.536 *	1			
	Cd	−0.174	−0.160	0.249	0.113	1		
	Pb	−0.276	−0.157	0.184	0.190	0.839 **	1	
	As	0.632 **	0.690 **	0.334	0.536 *	−0.370	−0.288	1

* Significance level at $p < 0.05$; ** remarkable significance level at $p < 0.01$.

Regarding significance, Cr and Ni, Ni and Pb, Cu and Cd, and Pb in the soil near Smeltery A showed a significant positive correlation; Ni and Cu and As, and Cd and Pb showed a very significant positive correlation. There is a significant positive correlation between Cu and Zn, and Zn and As in the soil near Smeltery B; Cr and Ni, Zn, As, and Ni and Cu, Zn, As, and Cd and Pb have a very significant positive correlation. In terms of the correlation coefficient and significance, it can be shown that multiple heavy metals in the cultivated soil near the two smelters are polluting to different degrees [25,26]. These results indicate that there was more than one heavy metal pollution source at the soil sampling site, which might be from exhaust gas, dust, and other pollutants from smelteries.

In multivariate statistical analysis, PCA was used to further analyze the relationship and source of heavy metals. The analysis results show that the two factors extracted by PCA in Smeltery A could explain 67.663% of the total variance of the data, as shown in Table 4. According to the orthogonal values of the rotated factor load matrix, Ni, Cu, Cd, and Pb were closely related to the first principal component (PC1), accounting for 35.5% of the total variance, while Cr was mainly distributed in the second component (PC2), accounting for 32.2% of the total variance.

Table 4. Eigenvalues, contribution rates, and component matrix of principal components.

Smeltery	Parameter	Component	1	2	3	4	5	6	7
Total variance interpretation of Smeltery A	Initial eigenvalues	% of variance	2.978	1.758	0.95	0.673	0.365	0.155	0.12
		Cumulative %	42.549	25.114	13.575	9.609	5.218	2.219	1.716
		Total	42.549	67.664	81.239	90.847	96.065	98.284	100
	Extraction sums of squared loadings	% of variance	2.978	1.758					
		Cumulative %	42.549	25.114					
		Total	42.549	67.664					
Component matrix a of Smeltery A	Component		Cr	Ni	Cu	Zn	Cd	Pb	As
		1	0.451	0.843	0.816	0.409	0.603	0.755	0.545
		2	0.71	0.392	−0.124	−0.284	−0.752	−0.37	0.549
Total variance interpretation of Smeltery B	Initial eigenvalues	% of variance	3.4	2.106	0.586	0.404	0.301	0.144	0.059
		Cumulative %	48.565	30.088	8.376	5.767	4.305	2.052	0.847
		Total	48.565	78.653	87.029	92.796	97.101	99.153	100
	Extraction sums of squared loadings	% of variance	3.4	2.106					
		Cumulative %	48.565	30.088					
		Total	48.565	78.653					
Component matrix a of Smeltery B	Component		Cr	Ni	Cu	Zn	Cd	Pb	As
		1	0.851	0.942	0.645	0.773	−0.227	−0.226	0.82
		2	−0.09	0.072	0.489	0.372	0.916	0.91	−0.221

These results were consistent with Pearson's correlation analysis results, shown in Table 4. The factors in PC1 had certain homology. However, not all heavy metals can be distributed in one component. For example, As and Zn were mainly related to PC1 and partly related to PC2, indicating that all metals may be controlled by more factors. Cr in PC2 was separated from other heavy metals, showing that Cr mainly came from non-human local natural resources. Borůvka et al. also found that Cr and Ni in soil were mainly derived from the soil parent material [15]. In the principal component analysis of Smeltery B, the contributory ratio of the first two principal components was 48.565% and 30.088%, respectively, and the cumulative contributory ratio was 78.653%. PC1 was Cr, Ni, Cu, Zn, and As, accounting for 47.8% of the cumulative variance, while PC2, composed of Cd and Pb, was significantly separated from PC1, indicating that the two components came from different sources.

3.4. Ecological Risk Assessment of Heavy Metals in Soil

With the local soil background value as the evaluation standard [18,19], the index values of the potential ecological hazards of heavy metals in the cultivated soil samples near the two smelteries are shown in Table 5.

Table 5. Potential ecological risk assessment of metals in soil.

Site	E_r^i							RI
	Cr	Ni	Cu	Zn	Cd	Pb	As	
A0	3.30	11.96	20.73	1.25	156.09	10.55	62.22	266.10
A1	2.13	13.97	35.80	2.84	947.31	116.95	64.15	1183.15
A2	3.42	11.78	29.13	2.44	433.22	107.60	59.41	647.01
A3	2.86	11.47	34.80	2.96	354.95	20.20	50.67	477.91
A4	2.63	9.58	33.15	2.28	482.98	21.38	51.76	603.77
A5	2.66	9.33	22.41	1.54	335.66	11.32	47.44	430.37
A6	3.05	10.35	18.75	4.99	394.84	21.77	70.80	524.57
A7	2.09	8.77	15.86	1.83	308.80	18.48	60.20	416.04
A8	2.17	7.94	19.89	2.13	525.85	39.95	39.56	637.48
A9	2.06	7.42	16.44	2.03	239.36	20.34	37.54	325.19
A10	1.98	8.05	14.65	1.71	309.47	17.79	35.67	389.33
A11	3.06	12.45	28.19	1.47	312.01	21.27	54.93	433.39
A12	2.24	9.08	27.59	2.85	653.59	50.15	40.28	785.77
A13	2.17	9.07	18.40	2.39	379.41	16.35	64.64	492.44
A14	2.47	10.66	20.85	3.56	381.52	26.38	47.47	492.91
A15	2.54	8.11	24.90	3.78	751.06	32.70	36.65	859.75
A16	2.83	9.68	17.85	1.97	364.75	16.69	43.50	457.25
A17	2.94	11.44	27.71	3.85	560.96	39.70	51.91	698.50
B0	2.22	6.91	7.56	0.94	82.10	6.35	39.67	145.76
B1	1.98	6.65	10.38	1.11	128.91	7.53	49.40	205.97
B2	1.86	6.55	9.53	1.03	153.22	9.45	33.11	214.74
B3	1.84	6.68	21.44	1.77	419.02	66.73	29.36	546.84
B4	2.41	10.19	14.08	1.05	106.84	16.45	69.75	220.77
B5	3.16	11.73	26.17	3.48	143.88	11.75	63.29	263.47
B6	2.82	9.03	24.02	0.86	170.53	7.08	47.87	262.22
B7	3.72	14.12	26.32	3.12	175.96	12.24	74.18	309.64
B8	2.23	10.76	21.15	1.55	111.20	10.74	45.66	203.29
B9	2.35	8.31	15.92	0.83	162.79	6.91	45.95	243.06
B10	3.52	12.73	22.09	1.81	146.97	11.02	45.10	243.24
B11	2.45	8.15	13.18	1.30	175.74	10.00	40.60	251.42
B12	2.23	6.78	11.29	1.04	156.10	7.08	39.27	223.81
B13	2.67	9.52	13.91	0.97	152.34	7.15	47.88	234.44
B14	2.65	9.68	18.14	1.11	254.20	8.67	46.82	341.26
B15	2.59	12.55	23.77	1.80	156.06	13.80	49.53	260.11
B16	2.21	12.17	43.53	1.69	187.85	14.12	50.59	312.16
Average of Smeltery A	2.59	10.06	23.73	2.55	438.44	33.86	51.05	562.27
Average of Smeltery B	2.52	9.56	18.97	1.50	169.63	13.36	48.12	263.66

Note: E_r^i is the ecological response coefficient of heavy metal i; RI is the comprehensive potential ecological hazard coefficient.

According to the single coefficient of the Hakanson potential hazard index, it could be seen that the potential ecological risk of Cd pollution in the soil near Smeltery A was very high and that of As was high. The ecological hazard coefficients of Cr, Ni, Cu, Zn, and Pb were all less than 40, so these five heavy metals were graded as low ecological hazard. The ecological hazard of the seven heavy metals near Smeltery B was almost the same as that near Smeltery A [16,17]. The soil near Smeltery B is the most polluted by Cd, followed by As. The average E_r^i values of Cr, Ni, Cu, Zn, and Pb were all less than 40, indicating low potential ecological risk.

The potential ecological hazard of seven heavy metals in the soil near two smelteries was evaluated with a single factor. From Figure 4, among the seven heavy metals near Smeltery A, 72.22% of Cd was at the level of extremely strong ecological harm and 22.22% was at the level of very strong ecological harm. For As, 83.33% was at the level of moderate ecological harm. The overall pollution level of Smeltery B was relatively low. Among the seven heavy metals in the soil near Smeltery B, 58.82% of Cd was at the level of moderate ecological harm and 35.29% was at the level of high ecological harm. For As, 76.47% was at the level of moderate ecological harm.

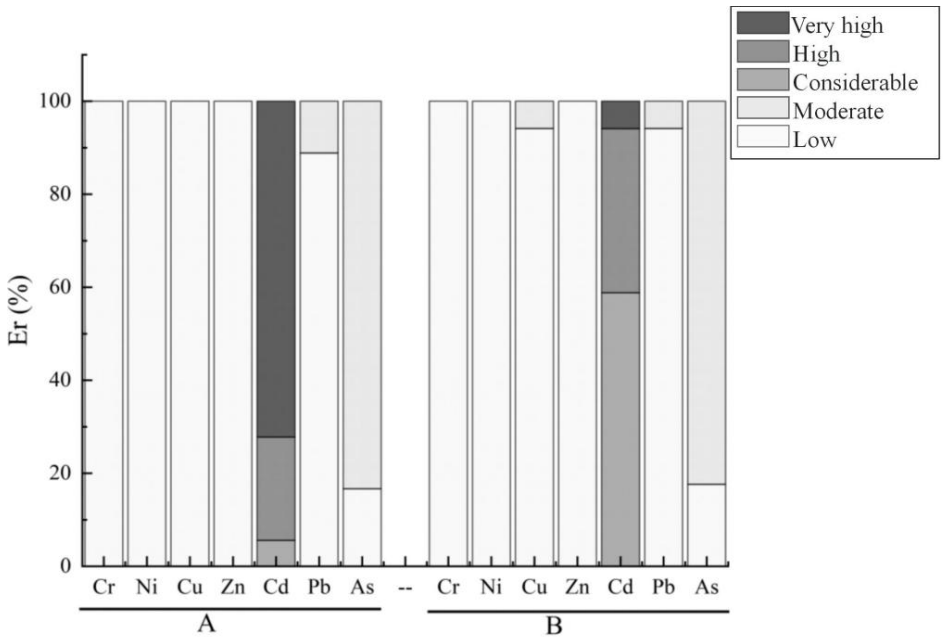

Figure 4. Distribution results of heavy metals in soil according to the single factor potential ecological risk index. A—Smeltery A; B—Smeltery B.

The comprehensive potential ecological risk (RI) assessment of multiple heavy metal elements can reflect the overall risks of the heavy metals around two smelteries. As seen in Table 5 and Figure 5, the average RI value of Smeltery A was greater than 300, which is generally at the level of high ecological hazard. The RI value of the most polluted sample near Smeltery A was 1183.15, and the level of strong ecological hazard is at a value of 600, so this sample with the highest pollution degree had a value 1.97 times higher than that of strong ecological hazard. The average RI value of Smeltery B was 263.66, and the overall ecological damage was at a medium level, while the degree of ecological damage at Smeltery B was relatively light. Among the samples taken near Smeltery B, about 23.53% were at the level of high ecological damage. The main heavy metal pollutants of soil near both smelteries were Cd and As, with Cd making the largest contribution.

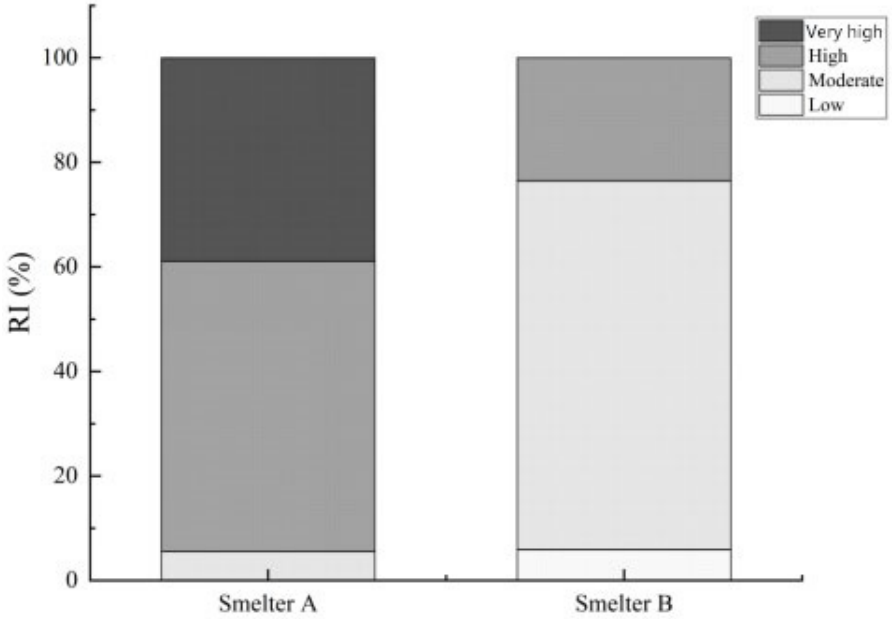

Figure 5. Comprehensive index evaluation results of potential heavy metal ecological risk.

Since the discovery of Cd in the early 20th century, Cd production has increased year by year. A considerable amount of Cd is discharged into the environment through waste gas, wastewaters, and industrial solid waste, causing pollution. The main sources of Cd pollution are lead–zinc ore, smelting and electroplating of nonferrous metals, and factories that use cadmium compounds as raw materials or catalysts [17].

4. Conclusions

In this study, the heavy metal content, spatial distribution, and ecological risks in soil surrounding two smelteries were investigated. The results show that the contents of heavy metals in the topsoil of farmland near Smelteries A and B exceeded the local soil background value, among which Cu, Cd, and As in the soil near Smeltery A and As in the soil near Smeltery B exceeded the standard screening value for soil pollution risk of agricultural land. According to the distribution map of heavy metal contents, it can be seen that As, Cd, Cu, Ni, and Pb have similar spatial distribution patterns. Among the seven heavy metals in the soil around the two smelters, Cd pollution is the most serious. Different wind directions, land application types, and transportation were the main reasons for the wide and uneven distribution of heavy metal pollution in soil. This study clearly provides insight that the pollution caused by smelteries near farmland poses hidden long-term hazards to humans. Therefore, it is urgent to carry out long-term monitoring of heavy metal smelteries and to rectify unqualified processes to ensure the healthy production of food crops. Targeted strategies should be implemented, and, even more importantly, control industrial point-source pollution to reduce the heavy metal pollution and ecological risks associated with the nonferrous metal smelting.

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