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Bioavailability, Sources, and Transfer Behavior of Heavy Metals in Soil–Crop Systems from a High Geological Background Area Impacted by Artisanal Zn Smelting in Guizhou Province, Southwest China

Honghong Ma [1,2,3,4,*], Chen Zhao [1,3,4], Li Zhang [1,3,4], Zhizhuo Liu [1,3,4], Fugui Zhang [1,3,4], Huiyan Wang [1,3,4], Fei Guo [1,3,4], Shiqi Tang [1,3,4], Zheng Yang [1,3,4] and Min Peng [1,3,4]

1 Institute of Geophysical & Geochemical Exploration, Chinese Academy of Geological Sciences, Langfang 065000, China; zfugui@mail.cgs.gov.cn (F.Z.); wanghuiyan@mail.cgs.gov.cn (H.W.); yzheng@mail.cgs.gov.cn (Z.Y.)
2 School of Earth Sciences and Resources, China University of Geosciences, Beijing 100083, China
3 Key Laboratory of Geochemical Cycling of Carbon and Mercury in the Earth's Critical Zone, Chinese Academy Geological Sciences, Langfang 065000, China
4 Geochemical Research Center of Soil Quality, China Geological Survey, Langfang 065000, China
* Correspondence: mahonghong@mail.cgs.gov.cn

Abstract: The environmental risk posed by heavy metals in agricultural soil is primarily influenced by their sources, bioavailability, and geochemical transfer behavior. This study focused on Weining County, a region in Guizhou province, Southwest China, with a high geological background and long-term impact from artisanal Zn smelting. Vertical soil profiles, crop, and rhizospheric soil samples were collected and analyzed for heavy metal concentration (As, Cd, Co, Cr, Cu, Hg, Ni, Pb, V, and Zn) including the total concentration and chemical fraction. The results revealed elevated concentrations of Cd (range: 0.7–6.9 mg·kg^{-1}), Co (range: 19.3–120.0 mg·kg^{-1}), Cu (range: 71.6–386.0 mg·kg^{-1}), Ni (range: 51.0–121.0 mg·kg^{-1}), and V (range: 310.0–721.0 mg·kg^{-1}) in all soil samples compared to the background values of Guizhou Province. Chemical fractionation analysis indicated that Cr, Ni, As, Cu, and Zn were predominantly present in the residual fraction, while Hg and Pb were predominantly found in the potentially bioavailable fraction. Cd exhibited the highest bioavailability, accounting for 58.5% of its total concentration. Enrichment factor analysis suggested that artisanal Zn smelting activities were the main sources of Cd, Pb, and Zn contamination. Furthermore, Cd, Pb, and Zn were found to be highly accumulated in the surface soil layer (0–20 cm). Notably, 90.0% of potato and 9.4% of maize grain samples exceeded the food hygiene standards for Cd concentration, posing potential health risks to consumers. The bioconcentration factor (soil-to-root) and translocation factor (root-to-grain) analyses indicated that maize roots had a higher tendency to accumulate Cd from the soil, while Zn and Cu showed a significant transferability from roots to maize grains. These findings offer valuable insights for devising heavy metal remediation strategies in similar areas.

Keywords: heavy metals; farmland soil; bioavailability; soil contamination; soil–plant transfer factor

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1. Introduction

Heavy metal contamination of farmland soil has become a significant concern worldwide. This issue not only compromises the quality of agricultural products but also presents potential toxic risks to both the ecological environment and human health [1,2]. Of particular concern are certain toxic elements that tend to accumulate in the human body, posing severe health risks. For instance, exposure to As can lead to cardiovascular disorders and other systemic problems, and in the long term, it may even contribute to the development of cancer [3]. Lead and Cd have been linked to various health issues such as blood and bone diseases, kidney dysfunction, nervous system disorders, and cardiovascular ailments [4].

Heavy metals in soil originate from both anthropogenic activities, such as metal mining and smelting, factory emissions, and sewage irrigation, as well as natural processes like the weathering of rocks and volcanic eruptions [5,6]. Generally, heavy metals from anthropogenic sources serve as the primary contributors to soil pollution [7], as they exhibit a higher mobility compared to those from geogenic origins [8]. Soil pollution caused by anthropogenic activities is challenging to reverse due to the low degradability, high concealment, and ease of enrichment of heavy metals [9,10]. Therefore, it is essential to assess the contamination level and identify the sources of heavy metals in the soil to develop appropriate remediation methods and control regulations.

In comparison to the total concentration of heavy metals in soil, the chemical fraction (the relative existence of a metal in different chemical forms) can provide greater insights into their bioavailability and release potential under various conditions [11]. Heavy metals in the soil exist in several chemical fractions with varying solubility, including the water-soluble fraction (F1), ion-exchangeable fraction (F2), fraction bound to carbonates (F3), fraction bound to humic acid (F4), fraction bound to Fe-Mn oxides (F5), fraction bound to organic matter (F6), and the residual fraction (F7) (occluded by mineral structures) [11]. Except for F7 of heavy metals, the other fractions are generally considered to be bioavailable or potentially bioavailable [12]. Therefore, exploring the bioavailability of heavy metals in the soil is crucial for a comprehensive understanding and prediction of their mobility and toxicity.

Since the 17th century, artisanal zinc smelting activities using indigenous methods have been extensively carried out in the northwest of Guizhou Province, particularly in Weining and Hezhang Counties, due to the presence of abundant mineral resources [13,14]. By 2002, Hezhang County alone had thousands of operational smelting furnaces [15]. However, these small-scale workshops often employed inefficient and low-quality smelting processes, leading to the discharge of substantial amounts of slag and wastewater into the surrounding environment without proper treatment measures [15,16]. Concerns about environmental pollution prompted the government to phase out manual zinc smelting activities starting in 2004 [16,17]. Nevertheless, studies have revealed that the soil, air, and water in Weining and Hezhang areas remain significantly polluted by heavy metals [14,16,18,19]. It is important to note that the region is characterized by the widespread exposure of basic volcanic rocks (Emeishan basalt) and carbonate rocks, contributing to elevated geological background levels of heavy metals in the soil [7,20]. Unfortunately, most researchers have overlooked the impact of this geological background of heavy metal concentrations in farmland soil, which further complicates the restoration efforts. Given that maize and potatoes are the primary crops and staple foods for local residents in this area, ensuring their safety is of paramount importance. Therefore, there is a pressing need to investigate the ecological risks associated with heavy metals and their migration within soil–crop systems.

In this study, the total concentrations of heavy metals in crops (maize and potatoes), rhizospheric soils and vertical profile of soils were measured, and the chemical fractions of heavy metals in surface soils were analyzed. The primary objectives of this study were as follows: (1) to investigate the concentrations and bioavailability of heavy metals (As, Cd, Co, Cr, Cu, Hg, Ni, Pb, V, and Zn) in farmland soils in a high geological background area impacted by artisanal Zn smelting activities; (2) to distinguish the anthropogenic and natural sources of heavy metals in the soils; (3) to reveal the bioconcentration and translocation patterns of heavy metals in the soil–crop system.

2. Materials and Methods

2.1. Study Area

Soil–crop samples were collected from agricultural areas in Weining County (104°22′–104°29′ E, 26°49′–26°56′ N), located in southwest China's Guizhou Province. This region has a historical significance as an artisanal zinc smelting area, covering an approximate sampling area of 50 km^2 (Figure 1). While the production sites of the smelting activities are no longer visible, remnants such as manual zinc smelting tools and slag can still be found in some farmers' homes or at the edges of fields. The study area falls within the subtropical monsoon humid climate zone, characterized by an average annual temperature of 11.5 °C and an average annual precipitation of 909 mm. The landform predominantly consists of plateau mountains, with an average altitude of 2200 m. The primary soil parent rocks in this region are composed of Emeishan basalt, mainly consisting of pyroxene and plagioclase minerals (Figure 1). In this agricultural area, maize and potatoes are the main food crops cultivated and are essential components of the daily diet for local residents.

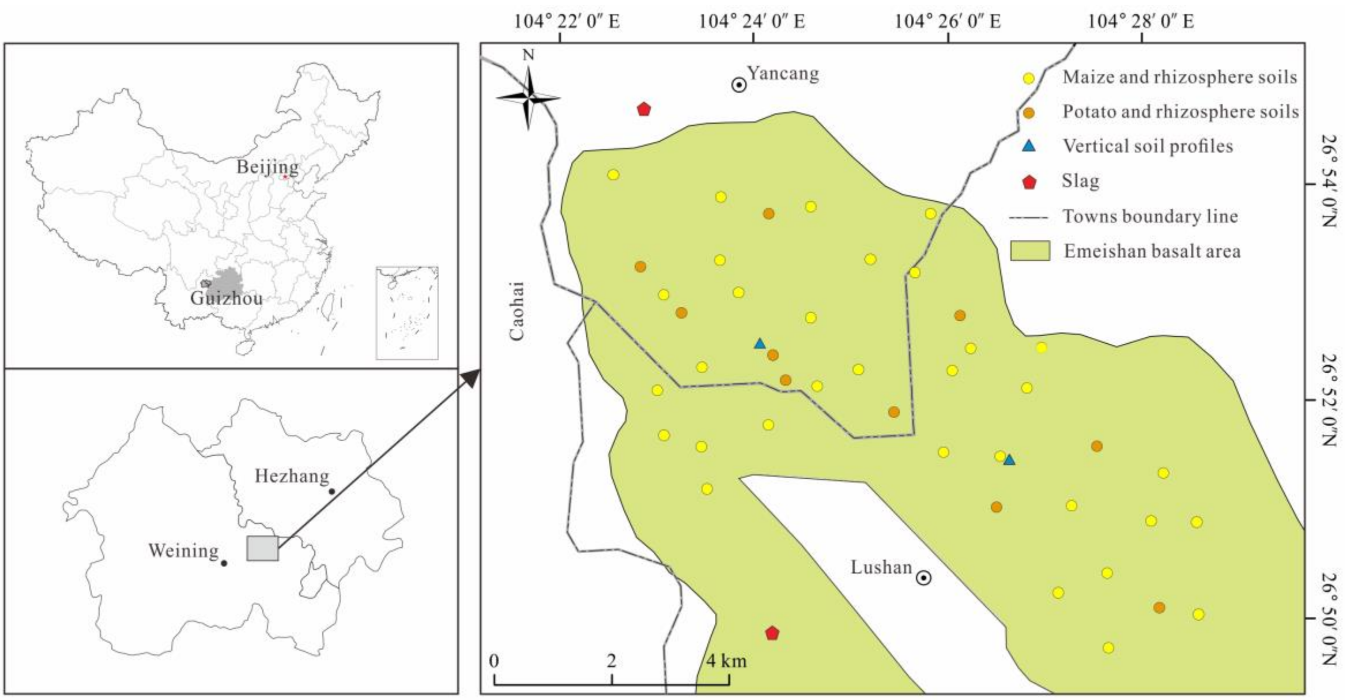

Figure 1. Geographical location and sampling sites of the study area.

2.2. Samples Collection and Pre-Treatment

A total of 42 pairs of crops (32 maize grains and 10 potatoes) and surface layer soil samples, and 2 soil vertical profiles were collected from agricultural fields in the study area (Figure 1). During the maize and potato maturity period (September to October), the plants were uprooted and the corresponding surface layer soil (0–20 cm depth) was collected with a stainless steel shovel. Four sub-samples (with an interval of 10–20 m) from each site were mixed together to obtain a single composite sample. Maize grains and potatoes were put into a nylon porous bag, among which 8 fresh maize plants were divided into root, stem, leaf, and grain samples with scissors. The soil vertical profiles down to 180 cm/190 cm deep were collected from bottom to top (1 sample/10 cm), and a total of 37 soil profile samples were collected. All soil samples were air-dried at room temperature (20–25 °C), then crushed with a wooden hammer and sieved through a 2 mm sieve. After sending them to the laboratory, 100 g of each soil sample was used for soil pH analysis, and the remaining samples were fully dried in a constant-temperature drying oven at approximately 60 °C, then crushed to 0.074 mm (200 mesh) and used for chemical analysis. Maize root, stem, leaf, and grain samples were rinsed with tap water and deionized water, then put into a drying oven at 60 °C for drying (about 24 h), and processed with a grain mill to 60 mesh for further analysis. Potato samples were made into a juice (or paste) and sent to the analysis room for further analysis.

2.3. Analytical Methods and Quality Control

2.3.1. The Total Concentrations of Heavy Metals

The total concentrations of Cr, V, Zn, and Zr in the soil powder samples were analyzed by X-ray fluorescence spectrometry (XRF; Advant XP, ARL, Geneva, Switzerland). Cadmium, Co, Cu, Ni, and Pb were analyzed in the digested phase (0.1000 g samples were put into a Teflon crucible and dissolved with a mixture of concentrated acid (HNO_3 + HF + $HClO_4$)) by inductively coupled plasma mass spectrometry (ICP-MS; iCAP Qc, Thermo Scientific, Waltham, MA, USA). Arsenic and Hg were analyzed in the digested phase (0.1000 g samples were digested with aqua regia (3:1 HCL/HNO_3)) by atomic fluorescence spectrometry (AFS; AFS-3000, Beijing Haiguang Instrument Co, Beijing, China). Soil pH was measured in a 1:2.5 soil/water (dioxide-free water) suspension with a pH meter. The soil organic matter concentration was determined by the volumetric method of potassium dichromate.

The total concentrations of As, Cd, Co, Cr, Cu, Ni, Pb, V, and Zn in the plant samples were analyzed by ICP-MS, and Hg was analyzed by AFS (using the microwave digestion process). The detection limits of As, Cd, Co, Cr, Cu, Hg, Ni, Pb, V, and Zn were 0.01, 0.002, 0.002, 0.05, 0.003, 0.01, 0.2, 0.02, 0.001, and 0.05 $mg \cdot kg^{-1}$, respectively.

2.3.2. Chemical Fractions of Heavy Metals

The chemical fractions of heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn) were extracted into seven defined fractions by a sequential extraction method. Heavy metals in the soils were successively extracted as the following seven fractions: water-soluble fraction (F1), ion-exchangeable fraction (F2), fraction bound to carbonates (F3), fraction bound to humic acid (F4), fraction bound to Fe-Mn oxides (F5), fraction bound to organic matter (F6), and residual fraction (F7). The detailed analysis and extraction steps of the chemical fractions can be found in [21,22].

2.3.3. Quality Control

The quality of chemical analysis (the accuracy and precision of data) was checked with blank samples, repetitive samples, and standard reference materials (GSS30, GSS31, GSS33, and GSS34 for soil samples, and GBW10011, GBW10012, GBW10021, and GBW10043 for plant samples from IGGE, China) during the analytical process. The results indicated a good agreement between the measured and certified values in reference materials, and the passing rate for accuracy was more than 99% and the qualified rate of repeatability inspection was more than 96.2%.

2.4. Enrichment Factor (EF)

The enrichment factor (EF) is based on the normalization of an examined element against a reference element. EF has been widely used in contamination source apportionment and assessments of soil or sediment [23,24]. EF was calculated by following equation [25]:

$$\mathrm{EF} = \left(\frac{C_n}{C_{reference}}\right) / \left(\frac{B_n}{B_{reference}}\right) \tag{1}$$

Aluminum, Fe, Mn, and Zr are generally used as reference elements [23,26–28]. In this study, Zr was used as the reference element because it was not disturbed by anthropogenic activities such as mining and smelting. Thus, where C_n represents the concentration of the examined heavy metal; $C_{reference}$ is the concentration of Zr in the soil samples; B_n is the reference concentration of the examined heavy metal; and $B_{reference}$ is the reference concentration of Zr. An EF value of 0.5–1.2 indicates that a metal is mainly controlled by the parent material and weathering processes, while a value of EF > 1.2 indicates that a metal is mainly derived from anthropogenic processes. In general, heavy metals in deep soils inherit the parent materials and are less disturbed by human activities. We considered that it is appropriate to use the values of metals in deep soils (the last 20 cm of soil vertical profiles) in this area as reference values. The reference values of As, Cd, Co, Cr, Cu, Hg, Ni, Pb, V, Zn, and Zr are 9.8, 0.3, 39.0, 168.5, 128.8, 0.149, 75.7, 29.0, 521.0, 121.0, and 350 mg·kg^{-1}, respectively.

2.5. Bioconcentration Factor and Translocation Factor

The bioconcentration factor (BCF) is defined as the concentration of heavy metals in the plant divided by the concentration of heavy metals in the soil, which reflects the ability of heavy metals to accumulate from soil to plant [29]. The translocation factor (TF) represents the ability of heavy metals to transfer from crop root to grain [29]. BCF and TF were calculated as follows:

$$\text{BCF} = \frac{C_{root}}{C_{soi}} \quad (2)$$

$$\text{TF} = \frac{C_{grain}}{C_{root}} \quad (3)$$

where C_{root}, C_{soil}, and C_{grain} are the heavy metal concentrations of the root, soil, and maize grain, respectively.

2.6. Statistical Analysis

All analytical data were analyzed using SPSS 19.0 software. The Shapiro–Wilk method was used to test the data for a normal distribution. The results indicated that the total concentrations of Cd, Co, Ni, Pb, V, Zn, and Zr in the soils conform to a normal distribution, while As, Cr, and Cu follow a log-normal distribution. However, Hg did not conform to either a normal or log-normal distribution. Data plotting and graphical processing were performed using Excel 2016 and CorelDraw X7 software, respectively.

3. Results and Discussion

3.1. Total Concentrations of Heavy Metals in Soils

The average total concentrations of As, Cr, Co, Cr, Cu, Hg, Ni, Pb, V, and Zn in the soils were found to be 7.0 ± 3.9, 3.5 ± 1.4, 50.7 ± 21.6, 139.4 ± 55.9, 167.0 ± 67.2, 0.090 ± 0.044, 79.6 ± 16.0, 39.8 ± 11.3, 466.0 ± 83.6, and 176.9 ± 34.3 mg·kg^{-1}, respectively (Table 1). With the exception of As and Hg, the average concentrations of the other heavy metals in the study area were higher than their corresponding background values in both the soils of Guizhou Province and China [30]. Notably, all soil samples exhibited elevated levels of Cd, Co, Cu, Ni, and V, surpassing their corresponding background values in the soils of Guizhou Province [30]. These findings indicate a significant enrichment of heavy metals such as Cd, Co, Cu, Ni, and V in the surface soil of the study area. Furthermore, the results reveal that 100% of the soil samples exceeded the risk screening value for Cd contamination, along with 97.6%, 78.6%, 33.3%, and 19.0% of samples exceeding the risk screening values for Cu, Ni, Cr, and Zn, respectively, as set by the Ministry of Ecology and Environment of the People's Republic of China [31]. This indicates a high risk of contamination to agricultural production and potential implications for human health. The pH levels of the soils were predominantly acidic, ranging from 4.4 to 8.0, with a mean value of 5.3 (Table 1). Additionally, the average concentration of organic matter (OM) in the soils was found to be 3.4% (Table 1).

Table 1. Statistical results of the total concentrations of heavy metals in the soils (mg·kg^{-1}).

n = 42	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	V	Zn	Zr	pH	OM [1] (%)
Minimum	1.7	0.7	19.3	70.2	71.6	0.028	51.0	13.1	310.0	86.8	200	4.4	0.9
Maximum	16.6	6.9	120.0	287.0	386.0	0.229	121.0	62.2	721.0	239.0	659	8.0	9.6
Mean	7.0	3.5	50.7	139.4	167.0	0.090	79.6	39.8	466.0	176.9	390	5.3	3.4
Median	5.8	3.4	50.2	126.0	149.0	0.082	76.9	41.2	457.5	184.0	365	5.2	3.3
Standard deviation	3.9	1.4	21.6	55.9	67.2	0.044	16.0	11.3	83.6	34.3	119	0.7	1.4
CV [2] (%)	55.0	41.6	42.7	40.1	40.2	48.7	20.1	28.3	17.9	19.4	30.6	14.1	40.3
Guizhou Province [3]	20.0	0.659	19.2	95.9	32.0	0.110	39.1	35.2	138.8	99.5	238	6.2	4.3
China [4]	11.2	0.097	12.7	61.0	22.6	0.065	26.9	26.0	82.4	74.2	256	/	/

[1] Organic matter; [2] Coefficient of variation; [3] Soil background values of Guizhou Province [30]; [4] Soil background values of China [30].

We then compared the concentrations of heavy metals in soil in the study area to other lead–zinc mining and smelting regions. According to Peng et al.'s 2015 survey in this area [32], the average concentrations of As, Cd, Cr, Cu, Hg, Pb, and Zn in the soil were 14.07, 2.04, 160.17, 125.67, 0.12, 62.83, and 260.00 mg·kg^{-1}, respectively. The current survey revealed higher Cd and Cu levels compared to previous research. The investigation of heavy metals in the soil around the Jinding Zn-Pb mining field in Yunnan exhibited median concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn at 29.4, 3.52, 57.3, 31.8, 0.18, 22.3, 115.3, and 233.1 mg·kg^{-1}, respectively [33]. In contrast, this study's soil exhibited significantly higher concentrations of Cr, Cu, and Ni, similar Cd levels, and comparatively lower levels of As, Pb, and Zn. Du et al.'s observations indicated that soil in mining-affected areas near Changsha had higher As (15.1 $\pm$ 4.1 mg·kg^{-1}) and Pb (51.2 $\pm$ 15.0 mg·kg^{-1}) concentrations than this study area [34], while displaying lower levels of the other seven heavy metals (excluding Hg). Furthermore, compared to findings in the nonferrous metal smelting area of Baiyin City [35], this study found higher concentrations of Co, Cr, Ni, and V, while Cd, Cu, Pb, and Zn concentrations were notably lower.

3.2. Bioavailability of the Heavy Metals in Soils

Chemical fraction analysis provides valuable insights into the mobility, release potentials, and bioavailability of heavy metals [36,37]. Figure 2 presents the average percentages of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in each fraction of the surface soil. To enhance clarity, F1 and F2 were combined as a single fraction called the exchangeable fraction (F1+2), as the concentrations of heavy metals in F1 were relatively low.

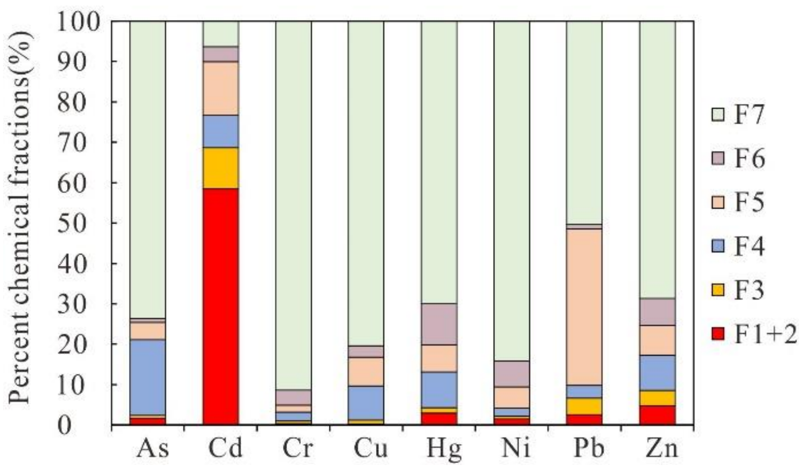

Figure 2. Percent of heavy metals in each fraction of the soils. F1+2: exchangeable fraction; F3: fraction bound to carbonate; F4: fraction bound to humic acid; F5: fraction bound to Fe-Mn oxides; F6: fraction bound to organic matter; F7: residual fraction.

In the soils, Cr, Ni, Cu, As, and Zn were predominantly found in F7, accounting for 91.3%, 84.1%, 80.4%, 73.7%, and 68.7% of the total concentrations, respectively. These fractions are considered to be non-available due to entrapment within the crystal lattice of minerals [38]. Conversely, in F1+2, Zn, Hg, As, Ni, Cu, and Cr accounted for 4.8%, 2.9%, 1.7%, 1.5%, 0.3%, and 0.3%, respectively. These fractions are considered bioavailable and easily absorbed by plants [22,38]. The presence of less than 5.0% of these six heavy metals in F1+2 indicates a relatively low biological activity and ecological risk. However, for Pb, approximately 47.0% was found in the potentially bioavailable fractions (F3, F4, F5, and F6), which are considered to be potentially available under strong acid conditions and could be absorbed by plants [22]. Additionally, 58.5% of Cd was distributed in F1+2, with only 6.3% present in F7. Cadmium and Pb were mainly detected in the exchangeable and potentially bioavailable fractions, highlighting the potential high risk they pose to food security and human health.

3.3. Sources of Heavy Metals Pollution

3.3.1. Enrichment Factor

Enrichment factor (EF) analysis was utilized to determine the sources of heavy metals in the soils, following the approach described by [23]. An EF value greater than 1.2 indicates a significant contribution from anthropogenic processes [23,28]. In this study, the concentrations of heavy metals in deep soils from the same area were considered as background values, and Zr was adopted as the reference element. As depicted in Figure 3, Cd exhibited the highest EF value, with an average of 9.65, indicating a substantial anthropogenic influence. Following this, Zn and Pb had average EF values of 1.33 and 1.28, respectively, also suggesting some contribution from anthropogenic sources. On the other hand, the average EF values of the remaining seven heavy metals were all below 1.20, indicating that Cu, Co, V, Ni, Cr, As, and Hg were primarily influenced by natural sources rather than anthropogenic activities.

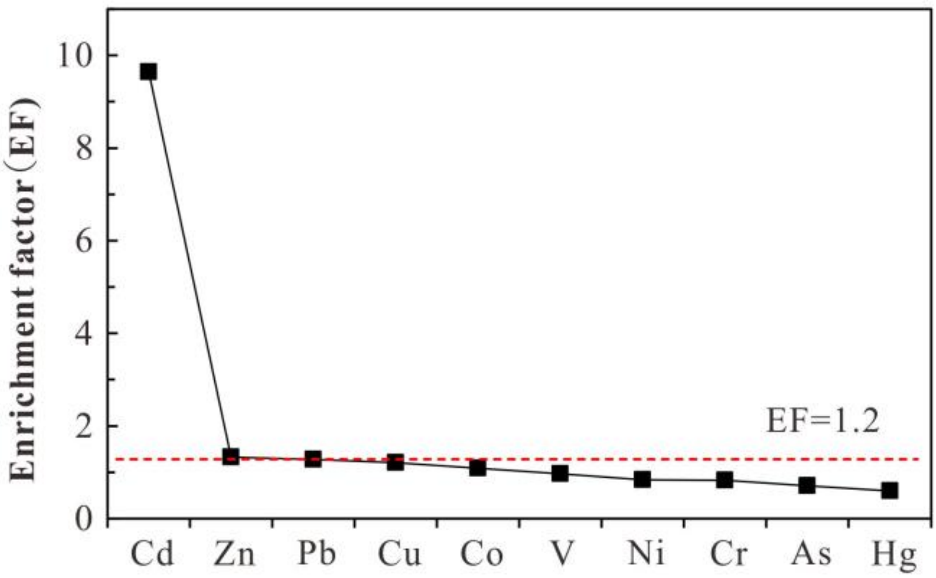

Figure 3. Enrichment factor (EF) of heavy metals in the soils.

3.3.2. Enrichment Horizon

The vertical distribution characteristics of heavy metals in soil profiles can provide insights into their sources, enrichment horizons, and migration abilities [39]. The concentrations of As, Co, Cr, Cu, Ni, and V exhibited minor variation trends, with slight decreases observed for Cu, Ni, and V, from the deep layers to the top layers in both profiles (Figure 4). These trends reflect natural weathering processes and indicate that these metals are less influenced by human activities. In contrast, the concentrations of Cd, Pb, and Zn in the soil profile samples ranged from 0.1 to 4.4 mg·kg^{-1}, 21.9 to 56.1 mg·kg^{-1}, and 104.0 to 209.0 mg·kg^{-1}, respectively. Notably, Cd, Pb, and Zn show significant accumulation in the surface soils (0–20 cm) (Figure 4), suggesting a strong impact from mining and smelting activities.

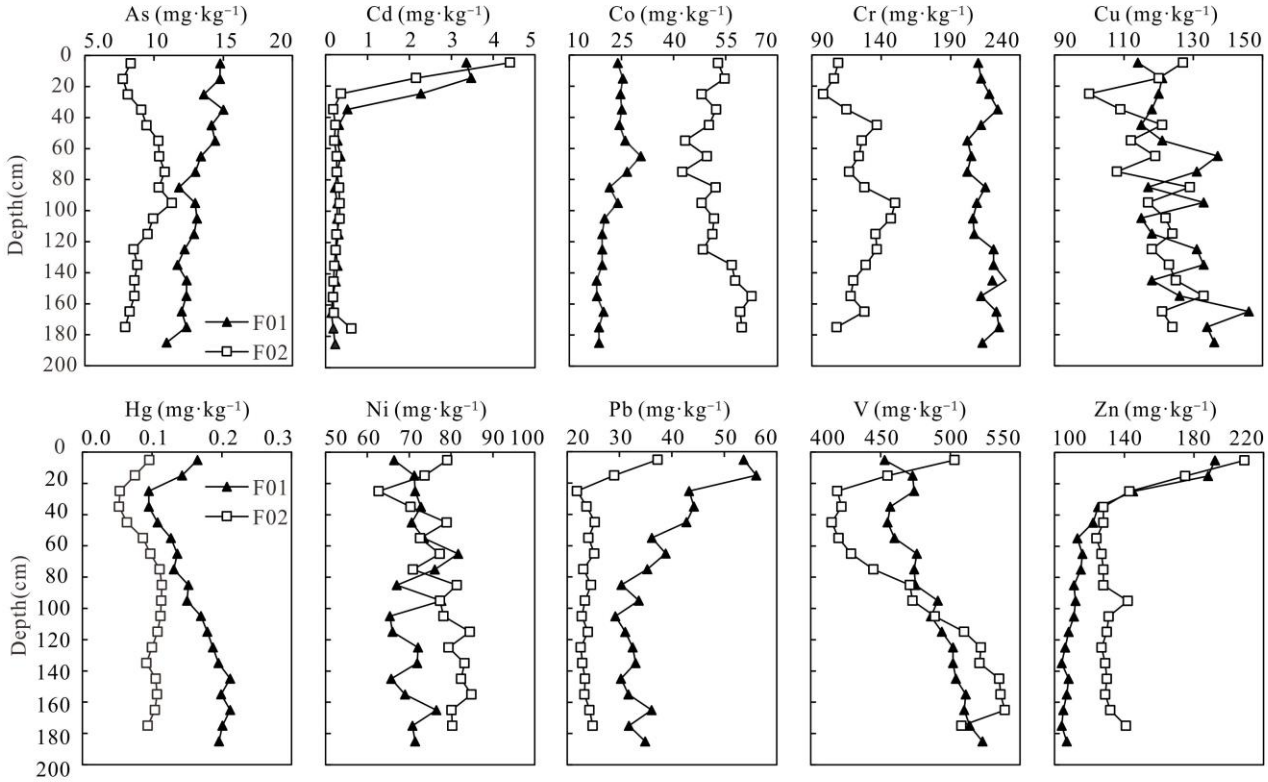

Figure 4. The concentrations of heavy metals in soil vertical profiles.

3.4. Total Concentrations of Heavy Metals in Maize and Potatoes

Maize and potatoes are the primary local food and economic crops, and the presence of heavy metals may directly impact the health of local residents. For maize grains, the average concentrations of heavy metals ranked in the order of Zn > Cu > Ni > Cr > Co > Cd > V > Pb > As (Table 2). The higher concentrations of Zn and Cu in maize grains can be attributed to their essential roles as plant nutrition elements [40]. Comparing the heavy metal concentrations in maize grains with the national food safety standard contaminant limits [41], it was observed that 9.4% of maize grains exceeded the contaminant limit for Cd (0.1 mg·kg^{-1}), while As, Cr, Hg, and Pb were all below the contaminant limit (Table 2).

For potatoes, the average concentrations of heavy metals ranked in the order of Zn > Cu > Ni > Cd > Co > V > As. A striking finding was that a significant portion of the potatoes (90.0%) exceeded the contaminant limit for Cd based on the national standard [41] (Table 2). These results further confirm the pollution of potatoes and maize grains by Cd in the study area. Notably, the over-limit rate of Cd in potatoes (90.0%) was significantly higher than that in maize grains (9.4%), indicating that rhizome crops, such as potatoes, are more prone to accumulate Cd. To reduce the risk of ecological pollution from heavy metals, it might be necessary to adjust the planting structure and consider alternative crop choices.

Table 2. Heavy metals concentrations in the maize grains and potatoes (mg·kg^{-1}).

		As	Cd	Co	Cr	Cu	Hg	Ni	Pb	V	Zn
Maize	*n* [1]	32	32	32	3	32	0	14	12	32	32
	Minimum	0.014	0.004	0.009	0.054	1.2	—	0.209	0.021	0.015	13.8
	Maximum	0.040	0.112	0.318	0.088	2.4	—	0.800	0.030	0.043	30.0
	Mean	0.020	0.047	0.049	0.072	1.8	—	0.393	0.026	0.028	21.2
	Standard deviation	0.006	0.027	0.067	0.014	0.4	—	0.168	0.003	0.007	3.3
	Limit [2]	0.5	0.1	—	1.0	—	0.02	—	0.2	0.5	0.1
	Over-limit rate (%)	0	9.4	—	0	—	—	—	0	—	—
Potato	*n*	10	10	10	0	10	0	1	0	10	10
	Minimum	0.002	0.093	0.026	—	0.7	—	0.297	—	0.004	3.9
	Maximum	0.007	0.190	0.650	—	2.2	—	0.297	—	0.005	8.2
	Mean	0.003	0.153	0.149	—	1.7	—	0.297	—	0.004	4.9
	Standard deviation	0.001	0.031	0.177	—	0.5	—	—	—	0.001	1.2
	Limit [2]	0.5	0.1	—	0.5	—	0.01	—	0.2	—	—
	Over-limit rate (%)	0	90.0	—	—	—	0	—	0	—	—

[1] *n*: the number of samples that were above the detection limit. [2] The national food safety standard contaminant limit in food [41].

As depicted in Figure 5, the concentrations of heavy metals in eight sets of maize samples, including the root, stalk, leaf, and corresponding grain, were measured. The results revealed significant differences in the concentrations of heavy metals among different parts of the maize plant. Specifically, As, Cd, Co, Cr, Ni, and V were found to be readily absorbed by the maize roots. On the other hand, Pb, Hg, and Zn were primarily accumulated in the maize leaves. It has been established in previous studies that Pb in leaves is mainly absorbed from the atmosphere [42]. It is essential to note that high concentrations of Pb (average: 3.9 mg·kg^{-1}) and Cd (average: 2.2 mg·kg^{-1}) were detected in the leaves. This finding raises concerns about potential risks to human health through the food chain, as the leaves are utilized as feed for livestock by local residents [15,43].

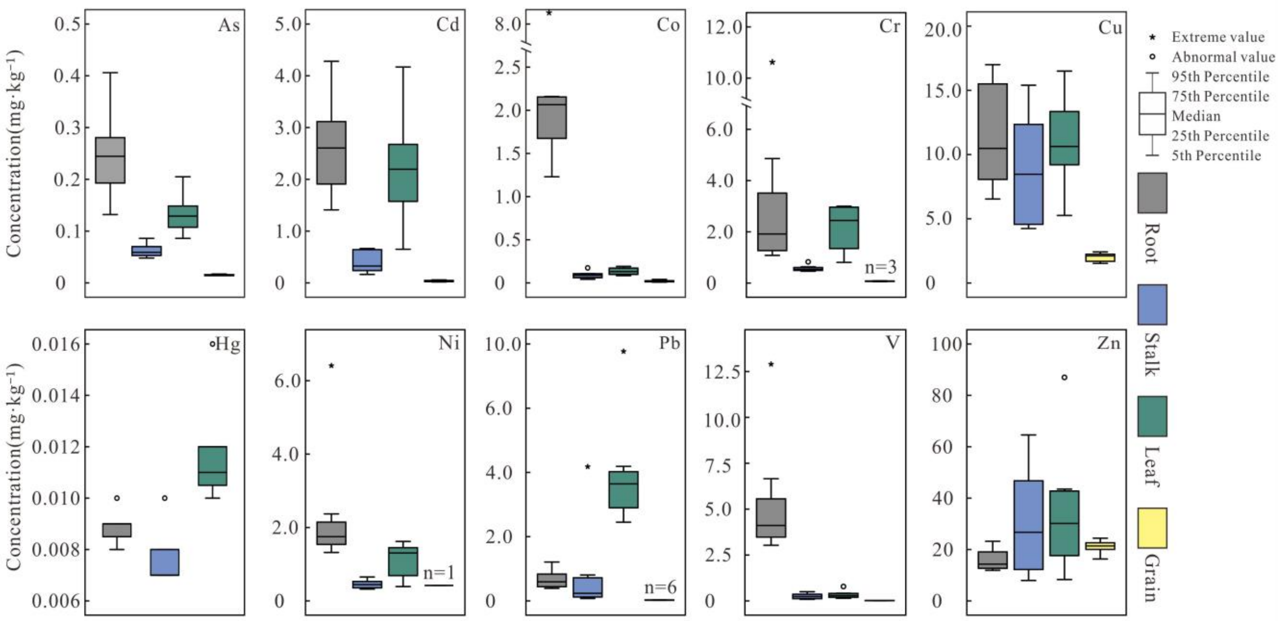

Figure 5. The concentrations of heavy metals in maize organs (*n* = 8, mg·kg^{-1}).

3.5. Transport of Heavy Metals in Soil–Maize System

The BCF is a commonly used metric to measure the ability of crops to absorb heavy metals from the soil [18,43]. As illustrated in Figure 6, the average BCF values for heavy metals follow the order: Cd (0.769) > Hg (0.115) > Cu (0.083) > Zn (0.081) > Co (0.051) > As (0.030) > Ni (0.028) > Cr (0.016) = Pb (0.016) > V (0.011). Cadmium showed the highest enrichment capacity for transferring from soil into maize roots, likely due to its high bioavailability in the soil (Figure 6). On the other hand, the average BCF values of Cu, Zn, Co, As, Ni, Cr, Pb, and V were all lower than 0.1, indicating that these metals had a limited uptake by maize roots from the soil. This finding aligns with previous studies [39,44]. It is worth noting that the root of the plant has various mechanisms to regulate and limit the absorption of metals from the soil.

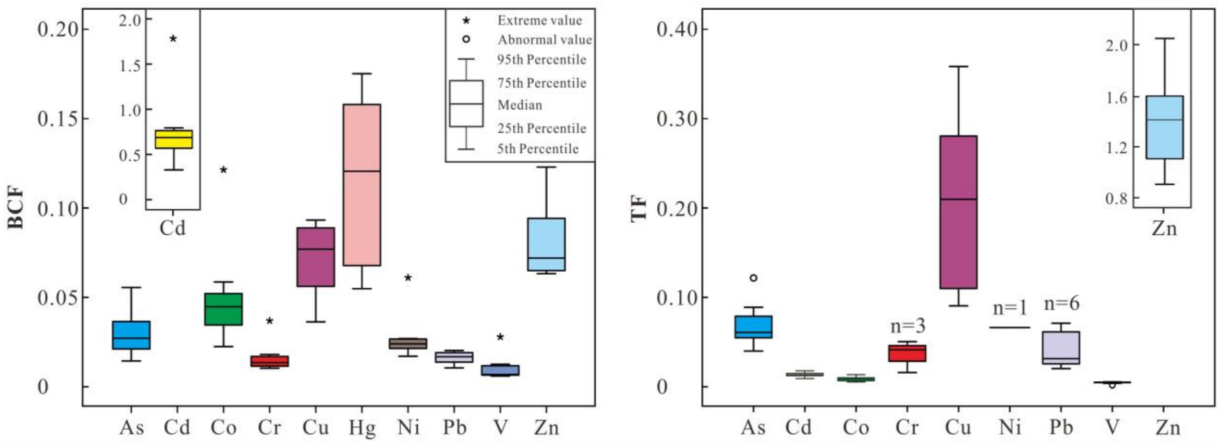

Figure 6. Bioconcentration factor (BCF) and translocation factor (TF) values for heavy metals (n = 8).

Mercury in maize grains was found to be below the limits of detection; thus, TF values for Hg were not calculated. As shown in Figure 6, the average TF values followed the order: Zn (1.398) > Cu (0.206) > As (0.068) > Ni (0.066) > Pb (0.040) > Cr (0.035) > Cd (0.013) > Co (0.008) > V (0.004). Zinc exhibited the highest transfer ability from maize roots to grains, which is consistent with previous findings [18]. Notably, the TF value of Cd was significantly lower compared to its BCF value, indicating that Cd was highly enriched in maize roots but had a low translocation capacity to grains. This observation helps to explain why the over-standard rate of Cd in maize grains is lower than in potatoes.

4. Conclusions

Despite the government's ban on smelting activities two decades ago, Cd, Pb, and Zn, which originated from past smelting activities, are still highly enriched in the surface soil (0–20 cm) of farmland. Moreover, alarming levels of Cd contamination were found in 90.0% of potato samples and 9.4% of maize grain samples. The concentrations of Co, Cr, Cu, Ni, and V in the soils were primarily derived from the parent material background (Emeishan basalts) and weathering processes. Over 80.0% of Cr, Cu, and Ni existed in the residue fraction, indicating a low risk of ecological pollution from these elements. In the soil–maize system, Cd demonstrated a high tendency to be absorbed by maize roots, but its translocation capacity from roots to grains was limited. On the other hand, Zn exhibited the highest transfer ability from maize roots to grains. In light of these findings, it is crucial to implement remediation measures to reduce heavy metal pollution in areas impacted by artisanal zinc smelting.

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