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Distribution Characteristics, Risk Assessment, and Source Analysis of Heavy Metals in Farmland Soil of a Karst Area in Southwest China

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Abstract: Soil environmental quality related to the residents' life, health, and safety, has been the hotspot issues in science of ecological environment protection. Evaluating the distribution characteristics, ecological risk, and source of heavy metals in farmland is important for protecting soil resources. The agricultural area of Lianhua town, Gongcheng County, Guilin is a typical karst landform. In response to the problem of heavy metal pollution and complex sources in the soil of this area, the characteristics and sources of heavy metal pollution in the soil profiles from farmland, abandoned land, and forest were studied using the single-factor index method, the geoaccumulation index (*Igeo*) principal component analysis (PCA) and positive matrix factorization (PMF) model. The results showed that: (1) that the contents of cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn) in the soil profile of the study area were higher than that of the soil elements background values in Guangxi. The total and available forms contents of all heavy metal elements exhibited the characteristics of accumulation in the surface profile; (2) among the six heavy elements, the contents of Cd were in a moderately to heavily polluted state. The contents of Cd in some soil profiles exceeded the control standard for agricultural land soil pollution. The contents of Zn and Ni were from slightly to moderately polluted in areas with frequent agricultural activities; (3) according to the PCA and PMF model, there were three main sources of heavy metals in the study area. Among them, Cd, Cu, Ni, and Zn are related to agricultural activities; the elements As, Cd, Cr, and Hg are closely related to geological background; Pb and Zn are mainly affected by atmospheric sedimentation of transportation. Agricultural activities and natural geological background are the main contribution sources of heavy metals in soil. Human activities are the main factors that cause the accumulation of heavy metals in soil. This research has theoretical guidance and practical significance for the prevention and control of soil heavy metal pollution and the protection of farmland environmental quality in the region.

Keywords: karst areas; soil profile; heavy metals; pollution characteristics; source analysis

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Citation: Ma, Y.; Ning, J.; Yang, H.; Zhang, L.; Xu, C.; Huang, C.; Liang, J. Distribution Characteristics, Risk Assessment, and Source Analysis of Heavy Metals in Farmland Soil of a Karst Area in Southwest China. *Land* **2024**, *13*, 979. https://doi.org/10.3390/land13070979

Academic Editors: Wojciech Zgłobicki and Evangelia Golia

Received: 29 March 2024
Revised: 14 June 2024
Accepted: 28 June 2024
Published: 3 July 2024

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1. Introduction

Heavy metals are a group of trace elements that pose a threat to the ecological environment and human health due to their high toxicity, difficulty in pollutant degradation, long retention time, and ability to be sustainably utilized by organisms and have become a hot

topic of attention [1–4]. Excessive quantities of heavy metals entering the soil environment will affect the physical and chemical properties of the soil and inhibit the activities of microorganisms in the soil, leading to a decline in soil quality and production capacity. Meanwhile, heavy metals can also be accumulated through the food chain of "soil-crops-human body", posing a hazard to human health [5–9]. In recent years, the evaluation of heavy metal pollution has attracted considerable research attention. Therefore, carrying out research on the characteristics of soil heavy metal migration and transformation, pollution status and ecological risk assessment is crucial for comprehensively recognizing the current situation of soil environmental pollution, guaranteeing the safety of agricultural products and preventing, controlling, and remediating heavy metal contamination [5,9–12].

Gongcheng County, located in the northeast of Guangxi, is a typical karst county, with a high geochemical background of heavy metal elements. The secondary enrichment of heavy metal elements during weathering and soil formation processes of carbonate rocks is the main reason for their high contents. The concentrated interference of industrial and agricultural activities will further exacerbate heavy metal pollution in the local area [13–19]. Soil heavy metals in karst areas do not degrade easily and tend to bioaccumulate in organisms [20,21]. Studying the mobility and transformation patterns of heavy metals in soil profiles in karst agricultural areas is crucial for guiding the safe use of arable land and ensuring food security through the restoration of arable land. Previous soil survey data showed that heavy metals in karst areas are characterized by centralized, large-area, and irregular pollution; however, there are few reports on heavy metal pollution characteristics, potential risks, and pollution sources in this area. Whether from the perspective of arable land safety management or heavy metal pollution prevention, it is necessary to explore the distribution characteristics as well as the sources of heavy metals in the soil of this area. In this study, we examined soil and plant leaves samples. This will assist in accurately determining the source of heavy metals in soil and transfer from soil to the plants. Our findings can provide more accurate inferences of the sources of heavy metals in the soil.

In the present study, through the investigation of heavy metals in soils in a typical agricultural county in Guangxi, we analyzed the distribution of eight heavy metals mainly including arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn) in the vertical profile soil of Gongcheng County's karst area, and evaluated the distribution characteristics and ecological risk of heavy metals in karst soils. The sources of soil heavy metals were analyzed by using the correlation analysis, the principal component analysis (PCA), and the positive matrix factorization (PMF) model. This study provides basic data and a research basis for the development of karst farmland soils to support the ecologically sustainable utilization of karst farmland.

2. Materials and Methods

2.1. Study Area and Samping

2.1.1. Study Area

The study area is located in Gongcheng County, Guilin City, northeastern Guangxi Zhuang Autonomous Region. The landscape within the county is mainly mountainous and hilly, with relatively flat alluvial land along the river banks. The rainfall is unevenly distributed across all seasons, with hot and humid summers and dry spells in spring and autumn, the annual rainfall is 1453.1 mm, and the annual average relative humidity is 74%. Gongcheng County is a typical karst county in Guangxi, with a karst area accounting for 48% of the total area of the county. The karst area runs through the entire Gongcheng County in a strip from northeast to southwest, and the exposed strata are mainly dolomite and limestone of the Devonian Carboniferous system (Figure 1). Gongcheng County is also an important agricultural county mainly with persimmon trees, plum trees, and other cash crops. The total contamination rate of farmland soil in the county is high; the main contaminating elements are Cd, As, Hg, Cr, and Pb (unpublished data). However, at present, the source of heavy metals in this area is still unclear.

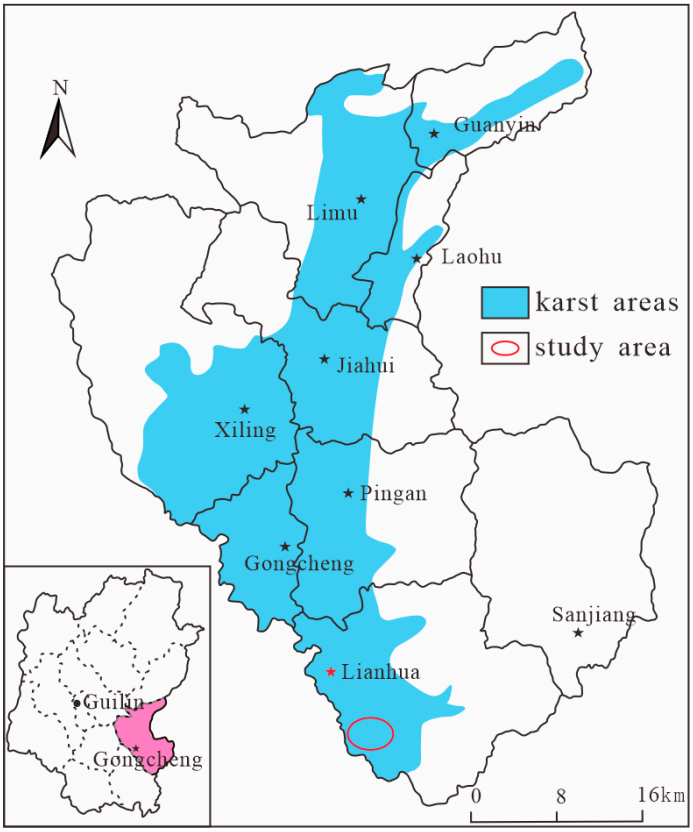

Figure 1. Location map of study area.

2.1.2. Sample Collection and Analysis

According to the soil survey data of the Agriculture Bureau of Gongcheng County in Guilin City, combined with geological background and pre-sampling research results, soil profile samples were collected from agricultural areas with excessive heavy metals in soil in June 2021. A total of three types of land use vertical profile soil were collected (Table 1). At least three representative plots were sampled from orchard and abandoned land to a depth of 100 cm, and a depth of 40 cm in the forest affected by bedrock. Samples were collected every 10 cm from 0 to 60 cm depth and every 20 cm from 60 to 100 cm depth. Soil water was collected at 25 cm and 50 cm in the orchard sample plots with a soil solution extractor. Firstly, a vacuum pump was used to form a vacuum from the soil solution extractor system, causing the extractor to be in negative pressure. Under negative pressure, soil water seeped into the extractor system, and under negative pressure, it took at least 24 h to fully extract the soil water into the collection bottle. Groundwater was collected at upstream and downstream spring sites in the cultivated areas.

Table 1. Characteristics of soil profile in the study area.

Profile	Parent Material	Location	Land Use Type	Depth (cm)
HS-O	limestone	hill foot	orchard land	100
HS-CK	limestone	hillside	secondary forest land	40
HS-HD	limestone	hill foot	abandoned land	100

Soil samples collected were brought back to the laboratory to pick out the fine roots and gravel, then sieved through a 2 mm mesh sieve and placed on kraft paper for air-drying; after air-drying, the samples were crushed with wooden hammers, ground, and then sieved through a 100 mesh nylon sieve; after sieving, all the samples were placed on colorless polyethylene film and mixed well before being placed in zip-lock bags and stored until analyzed.

2.1.3. Laboratory Analysis

Soil pH was determined using a soil–water ratio of 1:2.5, shaken at least 30 min and left to stand 30 min, and then measured with a SevenExcellence multiparameter tester (Quark Ltd., Nanjing, China). Soil organic carbon (SOC) was measured using the $K_2Cr_2O_7$-H_2SO_4 oxidation method [22]. Total N concentration was measured with the Semi-Micro Kjeldahl method. All the samples were digested by $HClO_4$-HNO_3-HCl, and then inductively coupled plasma mass spectrometry (ICP-MS, Thermo Fisher Scientific Co., Ltd., Bremen, Germany) was used to determine the total amount of the elements aluminum (Al), As, calcium (Ca), Cd, Cu, Cr, iron (Fe), magnesium (Mg), Ni, Pb, and Zn, inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo Fisher Scientific Co., Ltd., Bremen, Germany) for the determination of the total amount of the elements phosphorus (P) and sulfur (S), and atomic fluorescence spectroscopy for the determination of the total amount of the element Hg [22]. Diethylenetriamine acetic acid-calcium chloride-triethanolamine (DTPA-$CaCl_2$-TEA) was used to extract the available form elements in soil, and the inductively coupled plasma emission spectrometer iCAP6300 (Thermo Fisher Scientific Co., Ltd., Bremen, Germany) was used to measure Cd, Cu, Fe, Ni, Zn, and Pb concentrations [22]. Three replicates were performed for each soil sample.

2.2. Pollution and Risk Assessment Methods

2.2.1. The Single-Factor Index Method

The single-factor index method can show the degree of contamination of individual heavy metal elements in soil, which is an important parameter for the evaluation of soil environmental quality and is highly applicable to localized regional evaluation [23,24]. The calculation formula is:

$$P_i = \frac{C_i}{S_i}$$

where P_i is the single-factor pollution index of heavy metal i, C_i is the measured value of heavy metal i in a sample, and S_i is the soil standard of heavy metal i. The standard values refer to the indicator evaluation grading of the "Soil Environmental Quality Risk Control Standard for Soil contamination of Agricultural Land (Trial)" (GB 1568-2018) [25]. The standard is: when $P_i \leq 0.7$, it is good; when $0.7 < P_i \leq 1$, it is non-pollution; when $1 < P_i \leq 2$, it is mild pollution; when $2 < P_i \leq 3$, it is moderate pollution; when $P_i > 3$, it is heavy pollution.

2.2.2. Geocumulative Index (I_{geo})

The geocumulative index (I_{geo}) is commonly used to represent the degree of soil pollution and is a quantitative indicator for studying a geochemical standard for evaluating the degree of soil or sediment pollution, which takes full account of natural factors and has been commonly used by scholars since the late 1960s for evaluating soil heavy metal pollution [26,27]. The expression is:

$$I_{geo} = \log_2\left[\frac{C_i}{k \times B_i}\right]$$

where I_{geo} is the geoaccumulation index, C_i is the measured content of heavy metal i in soil (mg/kg), B_i is the background value of heavy metal i in the soil (mg/kg); k is the correction coefficient, generally taken as 1.5. The grading standard of I_{geo} is as follows: when $I_{geo} \leq 0$, it is no pollution; when $0 < I_{geo} \leq 1$, it is no pollution–moderate pollution; when $1 < I_{geo} \leq 2$, it is moderate pollution; when $2 < I_{geo} \leq 3$, it is moderate–serious pollution; when $3 < I_{geo} \leq 4$, it is serious pollution; when $4 < I_{geo} \leq 5$, it is serious–extremely serious pollution, and when $I_{geo} \geq 5$, it is extremely serious pollution. Since the deep soil is less affected by anthropogenic interference, the heavy metal content characteristics of the deep part (soil C layer) are mainly affected by the geological background; therefore, this paper takes the arithmetic mean of the heavy metal content of the soil in the C layer of Guangxi as the

background value, evaluates the contamination of the heavy metals in the profile of the study area in comparison with that in the geological background, and facilitates the search for the source of contamination.

2.3. Source Analysis Method

The obtained data were statistically analyzed using the analysis software Statistical Package Social Science (SPSS ver. 20.0; IBM Corp., Armonk, NY, USA) to principal component analysis (PCA). Graphs were plotted using the OriginPro 2022 program (OriginLab, Northampton, MA, USA). The correlations between the soil heavy metal and the soil chemical properties were analyzed by the Pearson correlation test. Positive matrix factorization (PMF) was used to analyze the sources of heavy metals (EPA PMF 5.0, U.S. Environmental Protection Agency Office of Research and Development, Washington, DC, USA).

3. Results

3.1. Heavy Metals in Soil Profiles

The pH value of secondary forest soil is 6.88–7.12, with an average value of 7.01. The pH of abandoned land soil ranges from 6.95 to 7.24, with an average value of 7.12. The overall vertical variation is relatively small, while the pH of orchard land soil is slightly acidic due to the influence of perennial human agricultural activities. The pH value ranges from 5.06 to 5.91, with an average value of 5.55. The pH shows a trend of first decreasing and then increasing in the vertical direction.

The contents of Cd, Cr, Cu, Ni, Pb, and Zn in each soil profile of the study area are higher than that of the background values of soil elements in Guangxi (Table 2) [28], while the content of As was similar to the elemental background values in Guangxi, the content of Hg was much lower than the background values, and Cd, Cu, Zn, and Ni contents were higher than those of the surface soils in Guangxi [27]. However, compared with the A-layer soil of limestone in northeastern Guangxi [29], the Cd and Hg contents in the study area were lower, except for the higher Pb and Zn contents in the HS-HD profile. All the heavy metal elements in the soil profiles in the study area showed the characteristics of surface (0–30 cm) accumulation (Figure 2). Except for the forest profile HS-CK, the vertical variation pattern of each element at a depth of 30–100 cm is not obvious, which may be related to the deep cultivation of the soil in the study area before planting fruit trees. Overall, the heavy metal elements in the study area are controlled by the natural high geological background, and human activities are the main influencing factors of heavy metal elements in the area.

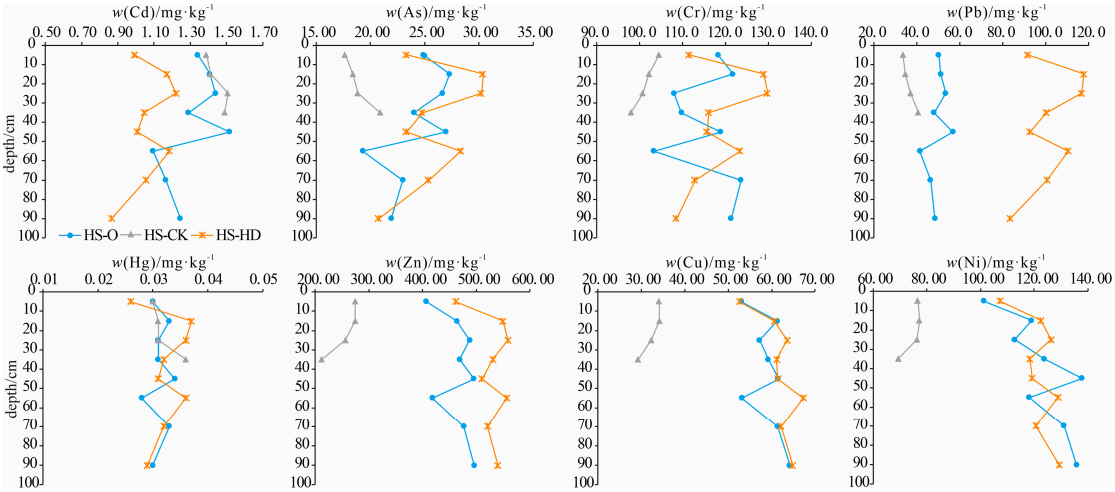

Figure 2. Distribution characteristics of heavy metals element content in soil profiles of the study area.

Table 2. The average content of heavy metals in the soil profile of the study area (mg/kg).

Profile	Cd	As	Cr	Pb	Hg	Zn	Cu	Ni
HS-O	1.31	24.25	115.63	49.53	0.03	464.33	58.89	122.47
HS-CK	1.45	18.96	101.40	36.54	0.03	254.54	32.47	74.87
HS-HD	1.07	25.83	118.41	101.76	0.03	528.74	61.72	121.58
Guangxi topsoil [27]	1.05	23.70	112.90	42.40	0.23	110.50	29.30	37.70
Background values of soil elements in Guangxi [28]	0.18	24.80	86.30	23.60	0.18	83.30	31.80	30.30
A layer of limestone soil in northeastern Guangxi [29]	3.25	32.92	135.77	49.63	0.23	324.87	55.80	78.86

The contents of available elements in each soil profile under different land use types in the study area were characterized by significant variations compared with their corresponding total contents of heavy elements (Figure 3). The contents of available elements in the soil profile also showed a certain surface accumulation in the soil profile, gradually decreasing from the surface layer to the deeper layer. The content of available elements decreases significantly from the 0–40 cm soil layer, and the content of available elements below 40 cm tended to be stabilized. Different land use types were compared; it was found that land use types have a significant impact on the available content of elements. The content of available Cd, available Cu, and available Ni in the native forest soil profile was higher than that in the orchard and abandoned profiles. The content of available Pb and available Cu in the orchard profile is the lowest, and the available Pb content in abandoned land is significantly higher than the other two types of profiles. The available content of Cd in the HS-CK profile is as high as 0.42 mg/kg, which exceeds the soil environmental quality screening value.

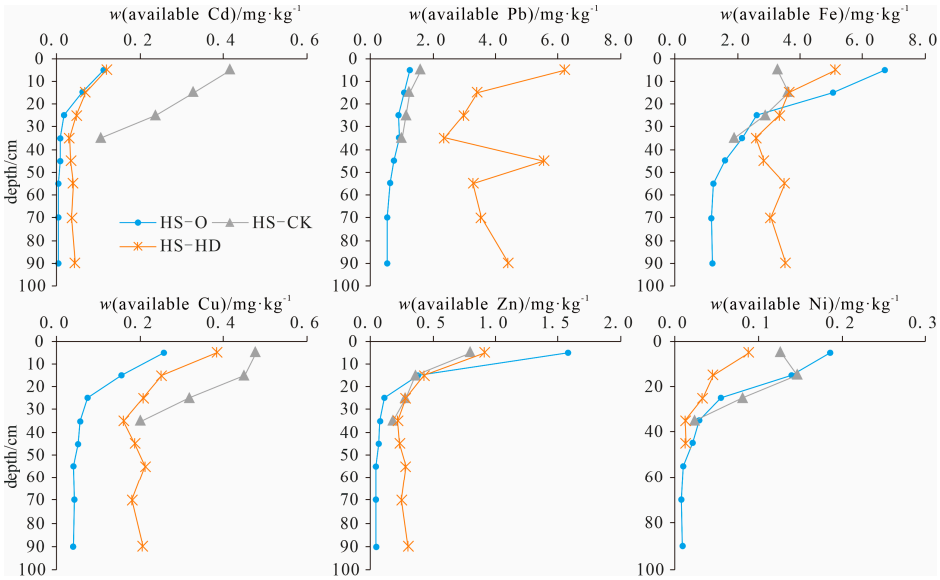

Figure 3. Distribution characteristics of available elements in soil profile of study area.

3.2. Pollution and Risk Assessment

3.2.1. Evaluation Results of Single-Factor Index Method

According to the factor index method classification standard for heavy metals, the distribution of heavy metals in each profile is shown in Figure 4. The content of Cd in the soil of the study area was in a moderately to severely polluted state, while Zn and Ni, except for the native profile HS-CK, were in a mildly to moderately polluted state. The remaining heavy metal elements were in a non-polluted state in the profile of the study area. The distribution of vertical contamination of heavy metals in the profiles was not obvious except for the primary profile HS-CK, which had a clear distribution pattern. The contents

of Cu, Zn, and Ni elements in HS-CK in the native profile were much lower than that in other profiles affected by human activities. In some HS-O profiles, the Cd content in the soil layer of 10–50 cm exceeded the risk control value and reached 1.14–1.36 times the control value, and this profile was also the most heavily polluted with Cd, which may be closely related to the agricultural activities in the orchard. The available surface content of Cd, Pb, Cu, Zn, and Ni elements in each profile of the study area is relatively high, especially in some profiles where the available content of Cd elements reaches the pollution level.

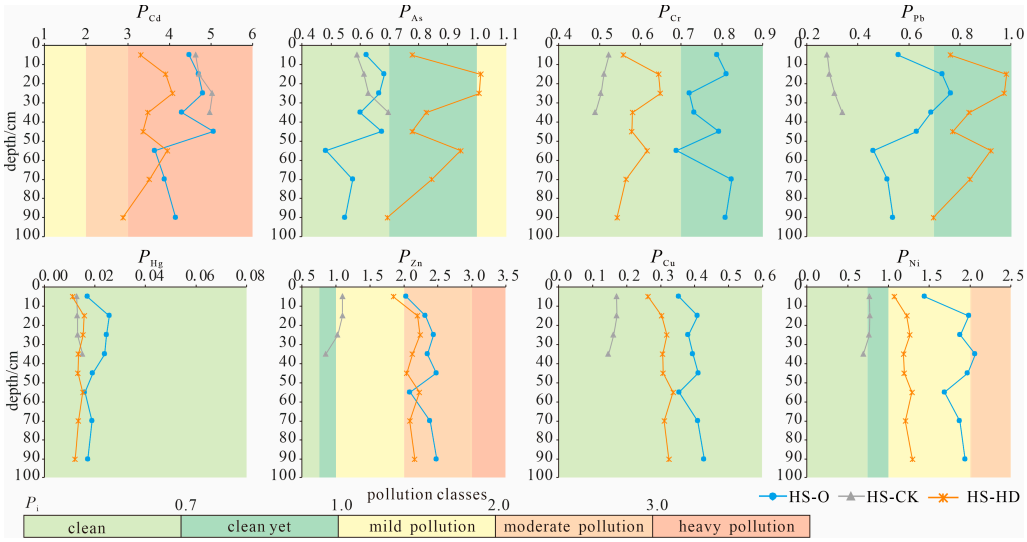

Figure 4. Distribution characteristics of heavy metal elements in soil profile based on single-factor index method.

3.2.2. Evaluation Results of Geoaccumulation Index

The geoaccumulation index (I_{geo}) is commonly used to evaluate the level of heavy metal pollution [30]. In this study, the content of soil elements in the deep layer (C layer) of Guangxi measured by the China Environmental Monitoring General Station [28] was used as the background value of natural soil, and the average I_{geo} of heavy metals in each group of profiles is shown in Table 3, from which it can be seen that relative to the background value of the study area, Cd reaches a moderately to heavily polluted level, Zn, Ni, and Pb were moderately polluted, Cu was mildly polluted in the area of frequent human activities, and the rest of the elements were non-polluted.

Table 3. Evaluation table index of geoaccumulation of soil profile in the study area.

Profile	Cd	As	Cr	Pb	Hg	Zn	Cu	Ni
HS-O	2.28	−0.62	−0.16	0.48	−3.17	1.89	0.30	1.43
HS-CK	2.43	−0.98	−0.35	0.04	−3.18	1.02	−0.56	0.72
HS-HD	1.98	−0.54	−0.13	1.51	−3.32	2.08	0.37	1.42

The results obtained from both the single-factor index method and the geocumulative index method showed that Cd in the soil of the study area was moderately to severely polluted, while Zn and Ni was mildly to moderately polluted.

3.3. Characterization of Elements in Groundwater and Soil Water

The results of elements in groundwater and soil water are shown in Table 4. Compared with the spring water HS-1 at the foothill spring and HS-2 exposed below the orchard, the contents of Cr, Cu, and Ni in the water after the spring water flows through the cultivated land show an upward trend. The heavy metal content in the surface layer (cultivation layer) of soil water in orchards was higher than that in the deep layer (50 cm) of soil water.

Compared with spring water, the content of heavy metal elements in soil water, except for Cd, showed a significant upward trend.

Table 4. Characteristics of heavy metal content in water in the study area (μg/L).

Sample	Cu	Pb	Zn	Cr	Ni	Cd	As	Hg	Location
HS-1	<0.09	<0.07	<0.8	1.52	1.08	<0.06	0.14	<0.07	foothill spring
HS-2	0.58	<0.07	<0.8	1.74	1.46	<0.06	0.14	0.076	orchard spring
25 cm	198.60	21.06	245.20	14.56	43.46	<0.06	1.67	10.81	soil water
50 cm	106.80	10.45	243.00	4.17	15.28	<0.06	0.44	0.76	

3.4. Source Analysis of Heavy Metals

3.4.1. Correlation Analysis

Correlation analysis was used to distinguish the degree of correlation between different indicators and can be used to preliminarily determine the source of heavy metals [19,23,31]. The correlation results of various heavy metal elements are shown in Figure 5. There was no significant correlation between Cd and Cr, Pb, Hg, Cu. Cd showed a significant correlation with Mg and As ($p < 0.01$) and extremely significant correlations between Cd and Zn, Ni ($p < 0.01$). In order to better determine the source of heavy metal elements, correlation analysis was conducted between heavy metals in the study area and major elements related to geological background including soil depth, Ca, Mg, Al, Fe, and S. The results showed that Cu, Ni, and soil depth showed a significant correlation ($p < 0.05$), while Hg and As showed a significant correlation with both Fe and Al. Generally, if there is a significant or extremely significant correlation between heavy metal elements, it indicates that heavy metals have the same source [23]. The leaching and deposition of major elements and soil depth also have a certain impact on the content of heavy metals, but there are certain differences in the degree of impact on different elements. Therefore, the above analysis can preliminarily indicate that the heavy metal sources in the study area have a certain degree of similarity. The soil in the study area may be affected by multiple heavy metal elements at the same time, with the characteristic of compound pollution.

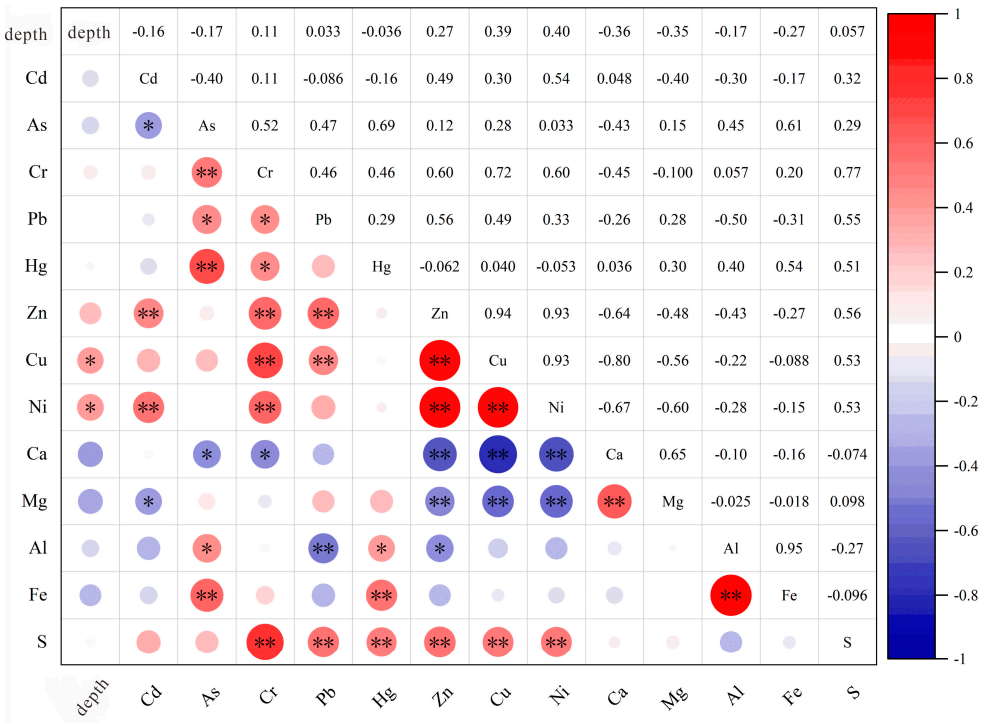

Figure 5. Correlation analysis of soil profile indexes in the study area. ** $p < 0.01$, * $p < 0.05$.

3.4.2. Principal Component Analysis (PCA)

To elucidate the source of elements in the soil, the contents of elements in the study area were analyzed using factor analysis, which reduces some observable variables with overlapping information. The KMO measurement test and Bartlett's sphericity test were performed on the soil sample data. Rotation matrix was used to analyze the sources of eight heavy metals. Four key factors with eigenvalues greater than 1 were identified, which were consistent with the actual situation and can reasonably explain the sources of pollutants. The contribution rates of pollution sources are shown in Table 5.

Table 5. Rotating composition matrix of heavy metals in the soil of the study area.

Heavy Metal	F1	F2	F3	F4
Cd	0.310	−0.120	0.923	−0.064
As	0.183	0.766	−0.438	0.234
Cr	0.726	0.571	−0.041	0.056
Pb	0.311	0.240	−0.098	0.908
Hg	−0.079	0.964	0.030	0.103
Zn	0.886	−0.044	0.255	0.365
Cu	0.965	0.081	0.031	0.198
Ni	0.928	−0.030	0.298	0.092
Eigenvalue	3.34	1.92	1.21	1.08
Contribution	41.70	24.03	15.15	13.47
Total Contribution	41.70	65.73	80.87	94.35

Extraction method: Principal component. Rotation method: Orthogonal rotation method with Kaiser standardization, with rotation converging after 6 iterations.

The main loads of factor 1 were Cu (96.5%), Ni (92.8%), Zn (88.6%), and Cr (72.6%). Figure 3 also showed that there is a significant difference in the content of Cu, Ni, and Zn between the agricultural and native soil in the study area, and the content of native soil was much lower than that in the agricultural area. Based on the analysis results of groundwater and soil water (Table 4), after the groundwater flows through the cultivated area, the Ni, Cu, and Cr in the water showed an upward trend. The content of Cu, Ni, and Zn in the surface (cultivation layer) soil water is also high, and Cu, Ni, and Zn have similar changes in each profile. Cu, Zn, Ni, and other elements play a key role in crop growth [32–35]. In order to ensure the healthy growth of fruit trees and the harvest of crops such as fruits, pesticides and fertilizers containing Cu, Zn, and Ni are often applied. Residual pesticides and fertilizers entering the soil cause heavy metal pollution; therefore, factor 1 can be determined as an agricultural source.

The main loads of factor 2 are Hg (96.4%) and As (76.6%). The uneven spatial distribution of heavy metals is mainly caused by natural factors [23,36]. From Figure 3, it can be seen that there is no consistent pattern in the content of each element in each group of profiles. But in the deep soil depth, element content is relatively close. The content of this group of elements was close to the surface soil value in Guangxi, slightly lower than the soil value in layer A of limestone in northeastern Guangxi. It can be determined that factor 2 is the natural geological background.

The main load of factor 3 is Cd (92.3%), and the content of Cd in the study area exceeds the risk value of agricultural soil pollution, far higher than the content of this element in the bedrock. During the weathering process of carbonate rocks, regardless of whether heavy metals are strongly depleted, heavy metals are significantly enriched in the soil profile [2]. The enrichment of Cd in carbonate weathered soil is largely similar to that of Ca during the weathering process of carbonate rocks [14–16,37]. Combined with the distribution characteristics of elements in various profiles and the correlation analysis between elements, Cd, Cu, Zn, and Ni elements related to agricultural activities have similar changes. Farmland is a typical area of interaction between natural processes and human activities [16], and human activities are an important influencing factor of Cd

content in the soil of the study area [38,39]. Therefore, factor 3 is a combination of natural geological background sources and agricultural sources.

The main load of factor 4 is Pb (90.8%). Previous studies showed that Pb was an indicative element of automobile exhaust and one of the most important types of traffic pollution [23,40]. The research area is mainly surrounded by agricultural activities, with relatively few industrial and mining activities. When engaged in agricultural activities, transportation tools are often used to transport agricultural products, fertilizers, etc., and agricultural machinery is used for weeding and plowing. The exhaust emissions from transportation vehicles usually contain a large amount of Pb [41]. The entry of soil Pb pollution is through atmospheric sedimentation [23]; therefore, factor 4 can be attributed to the source of transportation atmospheric sedimentation.

The contribution ratios of different pollution sources to heavy metal pollution in the soil profile of the study area were calculated by Orthogonal rotation method with Kaiser standardization. The highest contribution rate of agricultural activities to soil was 41.698%, followed by natural geological background (24.03%), composite pollution sources (15.145%), and transportation and atmospheric sedimentation (13.472%). Overall, the sources of heavy metals in the study area are relatively simple, mainly due to the weathering accumulation of carbonate rocks and human agricultural activity interference.

3.4.3. Positive Matrix Factorization (PMF)

Use the PMF model to analyze the source of heavy metals in the soil of the study area. The element contents and uncertainty were imported into the EPA PMF 5.0 software, and we used Formula (1) [42,43] to determine the uncertainty of the receptor data.

$$\mu_{ij} = 0.1x_{ij} + \mathrm{MDL}/3 \quad (1)$$

where μ_{ij} is the uncertainty value of the input data, x_{ij} is the input data value, and MDL is the method detection limit of each substance.

All signal-to-noise ratios (S/N) are greater than 7, and the default value is "strong". After running the model, combined with the element change characteristics and correlation analysis results, the number of operating factors of the element is adjusted multiple times. When the number of operating factors is set to 3, the Q value is 195.7, which is close to the theoretical Q value (190.7), and the difference between the Q value and the theoretical Q value is less than 10%. Except for Hg, R2 is greater than 0.75. The species and species contribution rates of various heavy metal components analyzed using the PMF model in the soil profile of the study area are shown in Figure 6. Factor 1 contributes to all heavy metal elements, and the contribution rates are Cd, Ni, Zn, Cu, Cr, Hg, As, and Pb in descending order. Among them, the contribution rates to Cd (68.97%), Ni (44.59%), Zn (42.88%), and Cu (38.71%) are relatively high. The heavy metal content in the cultivated layer (surface layer) of the study area, whether in soil or soil water, shows accumulation characteristics, and most element contents (excluding As and Hg) exceed the background values of Guangxi soil. Meanwhile, the content of agricultural activity areas is much higher than that of the original profile. Some studies have shown that heavy metal elements, especially Cd elements, from the soil-forming parent material are highly susceptible to agricultural activities [44,45]. The long-term use of pesticides and fertilizers not only makes the soil acidic but also gradually accumulates heavy metals, causing soil pollution. Previous studies have also shown that the accumulation of Cu and Zn is closely related to the long-term input of pesticides and fertilizers [18,46], so factor 1 can be attributed to agricultural sources.

The elements with a higher contribution rate in factor 2 are Hg, As, Cr, Ni, Cu, and Cd, with contribution rates of 64.81%, 61.07%, 57.68%, 34.06%, 32.13%, and 31.03%, respectively. The elements with a higher contribution rate of Hg, As, and Cr are close to or lower than the background value, and the $I_{geo} < 0$. Research has shown that the content of Cr and Ni in soil is mainly influenced by the parent material of the soil [18,21,44,47]. Therefore, factor 2 is attributed to a natural geological background source.

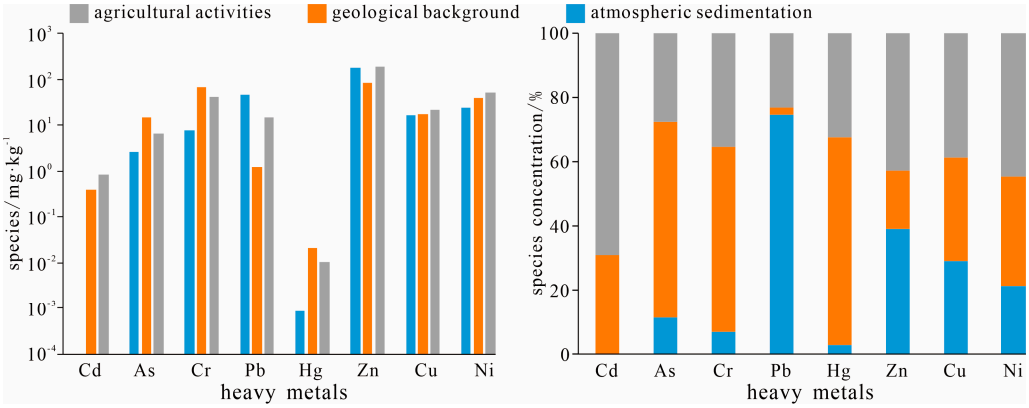

Figure 6. Source contribution for different elements by PMF.

The elements with the highest contribution rate in factor 3 are Pb, Zn, Cu, and Ni, with contribution rates of 75.48%, 38.92%, 29.16%, and 21.35%, respectively. This group of elements has a relatively high content in the profile. Considering that there are fewer industrial and mining activities around the study area, frequent agricultural activities, developed roads between farmland, and frequent use of agricultural machinery and transportation tools [46,48–50], the accumulation of Zn and Cu in the soil is related to the wear of tires during transportation and the braking of cars. Therefore, factor 3 is attributed to the source of traffic atmospheric sedimentation.

4. Discussion

4.1. Spatial Distribution and Pollution Analysis of Heavy Metals in Soil

The study area is located in a typical karst area in China. Previous studies have shown [16] that the contents of heavy metals, especially Cd in the soil of the carbonate rock area in Guangxi, are significantly higher than that of other regions in China. The content of Cd in the soil of the study area is at a high level in both orchard and forest, indicating severe pollution. In terms of spatial distribution, the overall content and available element content of heavy metals in the study area show a trend of surface (mainly 0–30 cm soil depth) accumulation, while the available elements of Cd, Cu, Ni, Pb, and Zn decrease downwards. The available element content in deep soil tends to be consistent. The high content of heavy metal elements in surface soil may be related to the activities of plant roots and microorganisms. The respiration of roots and microorganisms can lower soil pH, leading to the release of heavy metal elements [51]; deep soil is consistent with previous studies on the characteristics of "high background and low mobility" of elements in natural geological backgrounds [38,52,53]. In the study area, the heavy metal content in orchards and abandoned land with frequent human activities is higher than that in forest with low human activity. The pollution level in human activity areas is relatively high, indicating that heavy metal elements are easily affected by human activities, especially in the surface soil [39].

4.2. Sources of Heavy Metals in Soil

Comparing the results of two source analysis methods (Table 6), overall, the PCA and the PMF model source analysis results tend to be consistent. But there are some differences in the component spectrum and contribution rate of specific sources. The PCA extracted four factors, while the PMF model extracted three factors. Comparing the two analysis results, there are three main sources of heavy metals in the study area. The Cd element with high pollution risk is mainly influenced by geological background and human agricultural activities, which is consistent with the research results of relevant scholars on agricultural and karst areas in China [54–57]. The enrichment of Cd in the surface soil of carbonate matrix is the result of the dual effects of secondary enrichment and parent rock inheritance [57]. The use of pesticides and fertilizers in agricultural activities further

accumulates Cd in the soil [55,58]. The spatial distribution of Cu, Ni, and Zn elements in the soil of the study area shows that pollution only occurs in areas with frequent agricultural activities. Due to the presence of Cu, Ni, and Zn [59] in some pesticides, frequent use of pesticides and fertilizers during cultivation leads to the accumulation of heavy metals in the soil. Therefore, Cu, Ni, and Zn mainly come from agricultural activities. The content of As, Cr, and Hg elements is close to the background value, and there are Fe-Mn nodules in the soil of the study area. Studies have shown that Fe-Mn nodules are important factors affecting the enrichment of heavy metals in karst soil and are important carriers for heavy metal migration and enrichment [57,60–62]. Pb and Zn are mainly enriched in human activity-concentrated areas, while HD enrichment is more pronounced in the study area around roads. Research has found that automobile exhaust emissions, rubber tire wear, and brake wear can release Pb [59].

Table 6. Analysis results of two sources of heavy metals in the soil profile of the study area.

Analysis Method	Source Number	Heavy Metal	Pollution Source	Contribution/%
PCA	Source 1	Cr, Cu, Ni, Zn	agricultural sources	41.69
	Source 2	As, Cr, Hg	natural sources	21.03
	Source 3	Cd	agricultural and natural sources	15.15
	Source 4	Pb	traffic atmospheric sedimentation	13.47
PMF model	Source 1	Cd, Cu, Ni, Zn	agricultural sources	39.93
	Source 2	As, Cd, Cr, Cu, Hg, Ni	natural sources	26.93
	Source 3	Cu, Ni, Pb, Zn	traffic atmospheric sedimentation	33.14

Therefore, in the study area, Cd, Ni, Zn, and Cu elements are related to agricultural activities, while Hg, As, Cr, and Cd elements are closely related to natural geological backgrounds. Pb and Zn elements are mainly affected by transportation and atmospheric sedimentation, and agricultural activities and natural geological backgrounds are the main contributing sources of soil heavy metals. Human activities are the main factor causing the accumulation of heavy metals in soil. The research results can provide reference for the safe use of arable soil and the restoration of arable land to ensure food security in karst agricultural areas.

5. Conclusions

(1) Heavy metals in the study area all showed accumulation characteristics in the surface 0–30 cm soil layer with the contents of Cd, Cu, Cr, Ni, Pb, and Zn all being higher than the background values of soil elements in Guangxi. Both Cd in the soil profile and Zn and Ni in the agricultural activity area showed an accumulation trend compared to the background values of the C layer soil in Guangxi. The content of available elements gradually decreases from surface to deeper layers, the deep layer heavy metal showed high background and low mobility characteristics.

(2) The Cd elements were contaminated in all groups of profiles, with a moderate to heavy degree of pollution. Zn and Ni elements had mild to moderate pollution in areas with frequent agricultural activities, while non-agricultural activities were in a safe state. The enrichment of Cd, Zn, and Ni in agricultural activity areas increased the risk of soil pollution.

(3) The PCA-PMF analysis showed that there were three sources of heavy metals in the soils: natural sources and anthropogenic sources, including agricultural sources, natural geological background sources, and transportation atmospheric sedimentation sources. Among them, the Cd, Ni, Zn, and Cu in soils were mainly affected by agricultural activities. The Hg, As, Cr, and Cd contents in soil were closely related to the natural geological background. The Pb and Zn were mainly affected by atmospheric sedimentation during transportation. On the whole, agricultural activities and natural geological background were the main contributors of heavy metals in soil,

while human activities were the main factors causing heavy metal accumulation and enhanced heavy metal activity in soil.

Author Contributions: Investigation, Y.M. and C.X.; Methodology, J.N., C.H. and J.L.; Project administration, L.Z.; Writing—original draft preparation, Y.M.; Writing—review and editing, H.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the Guilin Key research and development project under Grant No. 2020010403, the Guangxi Key Research and Development Program under Grant No. GuikeAB22035004, the Guangxi Science and Technology Plan Project under Grant No. GuikeAD21196001, and the open foundation of the key laboratory of Ministry of Natural Resources/Guangxi Karst Dynamics Laboratory under Grant No. KDL&Guangxi202002.

Data Availability Statement: The data that support the findings of this study are available upon request from the corresponding author.

Conflicts of Interest: The authors declare that they have no conflicts of interest.

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