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Distribution Characteristics and Risk Assessment of Heavy Metals in Soils of the Typical Karst and Non-Karst Areas

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Abstract: To investigate the distribution characteristics and hazard levels of eight heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn) in karst soil with a high geological background of heavy metals, 32 and 40 surface soil samples were collected from limestone and clastic rock areas, respectively, in the northern part of Mashan County, Guangxi Province, a typical mountainous county dominated by primary industries in China. Geostatistical methods, Pearson's correlation analysis, the geo-accumulation index, and the potential ecological hazard index were applied to explore the influencing factors of those heavy metals and evaluate their potential contamination risks. The results show that (1) the levels of the eight heavy metal elements in the surface soils of karst areas exceeded the background values of soil for Mashan County, the background value of soil (layer A) in China, and abundance value of upper crust. According to the soil pollution risk screening values specified in the Soil Environmental Quality: Risk Control Standard for Contamination of Agricultural Land, the proportions of heavy metals in the soils of karst areas were ranked as Cd (100%) > As (90.6%) > Cr (84.4%) > Zn (68.8%) > Ni (37.5%). Meanwhile, the heavy metals in the soils of non-karst areas did not exceed the overall values for Mashan County, and Ni, Pb, and Zn did not exceed the overall national soil values. One-quarter of Cd in non-karst samples exceeded the risk-threshold screening value. There was a high degree of variation and a significant difference in the contents of heavy metal elements between karst and non-karst areas. (2) The element combinations of As-Cd-Cu-Hg-Ni-Pb-Zn and Cr in karst areas were characterized by the influence of carbonate rock parent material. The non-karst areas were characterized by Ni-Cu-Pb-Zn, As-Cr-Hg, and Cd assemblages, which were mainly influenced by the mixture of laterite parent materials, sand shale parent materials, and basic-rock residual materials, and that may be affected by element migration caused by soil erosion and anthropogenic activities. (3) Analysis of the geo-accumulation index showed that karst areas were generally found to be at the clean to light pollution level, except for in the areas whose samples exhibited medium/high pollution levels for Cd and Cr, with the Cd pollution being the more serious of the two. Small amounts of Cd and Cu were present in the non-karst areas at a light contamination level, while other elements were at the level of no pollution. (4) The results of the potential ecological risk index showed that Cd and Hg were the main ecologically hazardous heavy metal elements in the soils of the study areas. The potential ecological risk level in karst areas was much higher than in non-karst areas, especially for Cd, and was mainly influenced by the carbonate rock parent material.

Keywords: soil; heavy metals; karst area; non-karst area; potential ecological risk

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1. Introduction

Soil provides the substrate for terrestrial plants and animals to live on and is a natural resource for human survival and development. In environmental terms, the Environmental Protection Agency (EPA) lists eight elements as toxic heavy metals: arsenic (As), cadmium

(Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn) [1]. As a source and sink of heavy metals circulating in the environment, soil directly or indirectly affects ecosystem health. Excessive soil Cd and As can lead to plant growth disruption and crop yield reduction [2]; heavy metal infiltration in soil threatens groundwater quality [3,4] and enters the food chain, thus affecting human health. In recent years, with investigations and research work such as multi-target regional geochemical surveys and detailed soil pollution surveys, the soil with high geological background of heavy metals and other harmful elements formed by the enrichment under the natural environment has been gradually revealed [5–8]. Karst area composed of carbonate rocks is one of the typically high heavy metal background values areas that are affected by local geological structure. Previous studies have found that through carbonate rock area development, due to bedrock weathering processes triggering calcium, magnesium, and other elemental leaching, heavy metals show a certain inheritance or superimposed concentration effect. Heavy metals tend to be retained in the residue, with a consistent relative increase in the volume and content of heavy metals, meaning these can be found in areas with low bedrock contents, even after the development of the soil [9–13]. Compared to heavy metal pollution in agricultural fields caused by anthropogenic activities, soil pollution in areas with a high geological background of heavy metals is often characterized by high contents of heavy metals, large scales, and difficulty in intercepting and controlling pollution sources due to the influence of soil-forming parent material [14,15].

The elemental content of naturally occurring soils is mainly controlled by parent materials and processes of soil-forming. Due to the large area of Mashan County comprising carbonate rocks [16,17], the average content of heavy metals in soils is much higher than that in other regions of China [18,19]. The enrichment, spatial distribution and occurrence status of heavy metals affect human health at all times, as well as their ecological risks, are controversial and widely concerning. Some studies have concluded that although there is a high content of heavy metal elements in soils of carbonate rock areas, the proportion of effective states such as the water-soluble state is small and not greatly harmful to nature [20–22]. However, some related studies have also shown that effective states such as ion exchange and carbonate binding of heavy metal elements such as Cd can be high in carbonate rock areas and have high bioavailability [21,23]. According to recent studies, soils developed from different parent materials in the same carbonate background area are significantly different [11,15,24] and have a higher ecological risk under soil acidification [11], so type differences in parent material may be one reason for the differences in risk. Recently, more studies have been performed on the geochemical characteristics of the migration and enrichment of elements in weathering profiles or spatial distribution in karst areas [18,25–28], with an emphasis on the importance of studying the environmental risk aspects of soils in the high heavy metal background value areas that are affected by local geological structure. However, the scope of previous studies regarding the risk posed by heavy metals has been dominated by administrative divisions, but little consideration is made to the impact of different parent materials. It is necessary to study the healthy risk of soil heavy metals in karst and non-karst areas to accurately identify the current state of contamination and implement remediation measures.

There are numerous methods widely used to evaluate heavy metal pollution; for example, the Nemero integrated pollution index [29], the geo-accumulation index [30], and the potential ecological risk index [31]. To be able to accurately assess potential ecological risks, the specificity of the region and the applicability of the assessment methods should be considered first. The geo-accumulation index, which systematically takes into account the variation in background values for geological reasons and the influence of anthropogenic disturbance on the elemental content, can quite objectively assess the situation of excessive rate of heavy metals in soil and accurately reflect the accumulation degree of elements. The potential ecological risk index integrates the contamination levels of single heavy metal elements with heavy metal toxicity response coefficients in order to obtain the potential ecological hazard index after a weighted calculation, which can effectively characterize the impact potential of soil quality and heavy metals [32] and is therefore meaningful for health guidance. Liu et al. (2013) used the geo-accumulation index and the potential ecological hazard index to effectively reflect that Cd is the main ecological risk element in agricultural soils near sewage treatment plant in Guangzhou, China [33]. Zhao and Wang studied the enrichment characteristics and potential ecological risk characteristics of relevant heavy metals in the karst area of Yunnan, Guangxi, and Guizhou provinces, pointing out that Cd and Hg present the highest ecological risk [34].

In this study, we collected typical soils from the northern area of Baishan Town, Mashan County, Guangxi, China. We analyzed the content characteristics and influencing factors of heavy metals in soils under different soil-forming parent material conditions and applied the geo-accumulation index [30,35] and the potential ecological risk evaluation method [31] to evaluate the soil environmental quality, which are more reliable for the heavy metal content in sediments. Two evaluation methods were used to quantify the level of potential ecological risk of heavy metals, aiming at (1) improving the objectivity of soil environmental quality evaluation in karst background areas and (2) providing a scientific basis for the prevention and control of soil heavy metal pollution and ecological environmental protection.

2. Study Area

The study area is located in the north of Baishan Town, Mashan County, Guangxi (E 108.09°~108.02°, N 23.73°~23.85°) (Figure 1). The geomorphology of the area is characterized mainly by peak cluster depressions and poljes, the terrain is undulating, and the vegetation is dominated by natural broad-leaved forests. The annual temperature range is −0.7–38.9 °C, the average annual average is 21.3 °C; the annual frost-free period is 300–360 days, with the average being 343 days; rain is abundant, with the average annual rainfall being 1722 mm; and the distribution of the four seasons is uneven, with spring and autumn more arid and the summer flooded. Mashan is a typical mountainous county dominated by primary industries. The main income of the economy is agriculture, followed by forestry, animal husbandry, and fishery. The grain crops in Mashan County are mainly rice and corn, and the economic crops are mainly sugarcane, fruit, and peanuts. Therefore, soil erosion and excessive use of chemical fertilizers and pesticides may be the main exogenous import pathways of heavy metals in soil.

The stratigraphy and lithology of karst area mainly comprise the Carboniferous Maping Formation (C_2mp), dominated by light white thick layered limestone, with siliceous bands interspersed locally; the Permian Maokou Formation (P_1m), including a lithology of mainly gray limestone with a small amount of shale, and the lithology of the Qixia Formation (P_1q) comprises striated limestone and argillaceous limestone. The non-karst area comprises macker, iron bauxite, sand shale, and argillaceous limestone in Permian Heshan Formation (P_2h) and the Triassic Luolou Formation (T_1l), which contains limestone, siltstone, and shale [36–38]. The karst area is located on the east and west sides of the study area. The parent material is mainly limestone and its weathering residues or alluvial materials. The land use in karst area is mainly shrubs, dry land, and paddy fields. Conversely, the non-karst area is located in the middle part of the study area, and the parent material is comprises sand shale, sandstone residues, and alluvial deposit, and the land use is mainly forest and reservoirs.

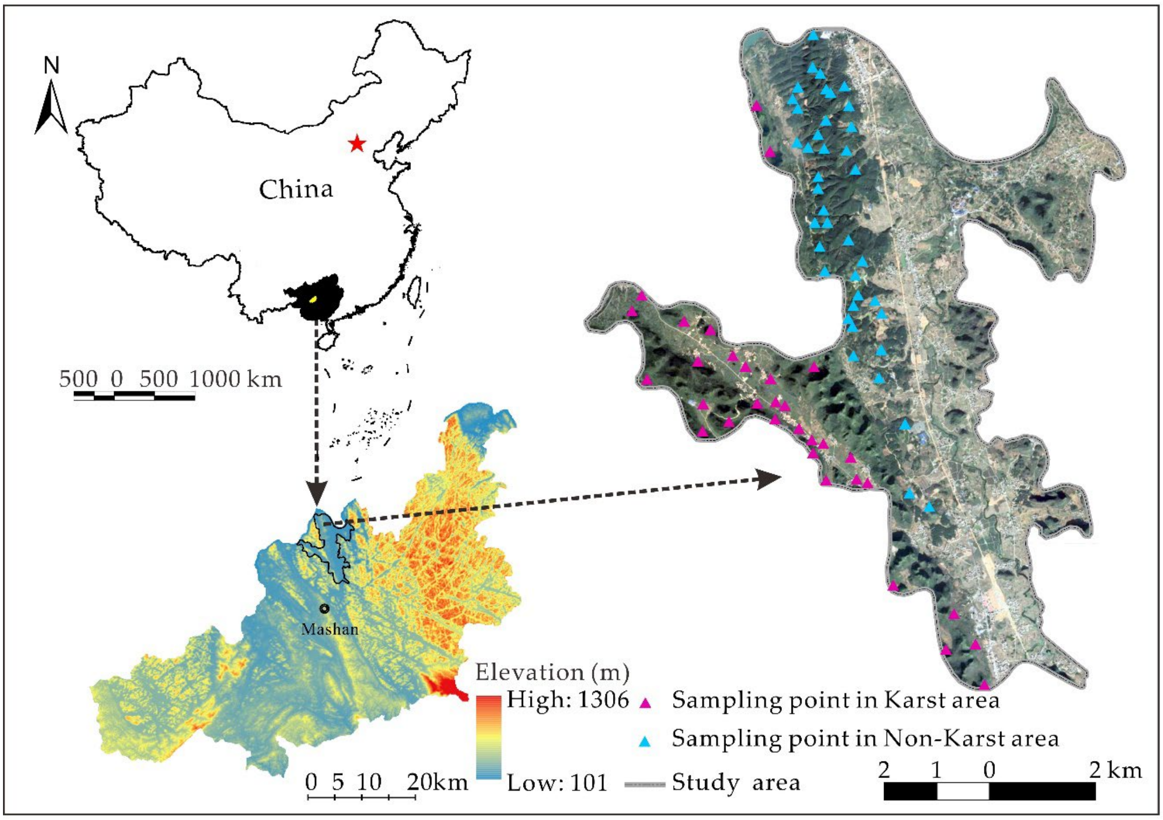

Figure 1. Location of the study area and distribution of sampling points.

3. Materials and Methods

3.1. Sample Collection and Processing

In this study, soil samples in karst area and non-karst area were collected in June 2017, and processing was carried out with reference to the specifications of the Land Quality Geochemical Assessment (DZ/T 0295-2016) [39]. The karst area (mainly limestone) and non-karst area (including mudstone, shale, and alluvial sediments) were selected as the research objects, surface soils (0–20 cm) were collected, an "X" or checkerboard shape was used to radiate 20–50 m, and 3–5 aliquot samples were collected to form a mixed sample. A total of 32 soil samples were collected in the carbonate rock area and 40 soil samples in the non-carbonate rock area; the sampling point distribution is shown in Figure 1. Soil samples were brought back to the laboratory to be naturally air-dried, and gravel, plant roots, and leaves were removed; then, the samples were poured into a 2 mm pore-size nylon sieve in a sample bag for testing.

The elemental content was tested after wet digestion and 5% HNO_3 volume fixation. The contents of As and Hg were measured using atomic fluorescence spectroscopy (AFS) after the soil sample was digested with aqua regia and reducted with Potassium Borohy. Cd, Cr, Cu, Pb, Ni, and Zn were determined by ICP mass spectrometry (PerkinElmer Inc., Waltham, MA, USA, NexION 300) after digestion of the soil samples with <0.074 mm particle size with an HCl-HF-$HClO_4$-HNO_3 mixture. The soil pH and organic matter were determined by a PHS-3C pH meter at a ratio of 1:2.5 (soil: CO_2 free water) and the potassium dichromate oxidation–ferrous ammonium sulphate method, respectively. Data quality monitoring was strictly controlled according to the specifications for a multipurpose regional geochemical survey (1:250,000) (DZ/T 0258-2014) [40]. Standard materials of soil (GBW07404 and GBW07406) covered all studied elements and were tested among every ninth sample, revealing that the average analytical errors were about 5%.

3.2. Evaluation Methods

3.2.1. Geo-Accumulation Index

The geo-accumulation index (I_{geo}) was first proposed by Müller [30,41]. It fully considers the changes to background values caused by natural geological diagenesis and other factors. I_{geo} is a quantitative indicator reflecting the degree of heavy metal pollution in a substance. It is calculated as

$$I_{geo} = log_2 \frac{C_i}{k \times S_i} \tag{1}$$

where C_i is the measured value of the heavy metal i; S_i is the background value of element i; and K is the correction coefficient, which is 1.5. In this study, the background value of soil heavy metals in Mashan County, Guangxi Province, was used as the geochemical background value for calculation. The grading criteria were as follows [42,43]: $I_{\text{geo}} \leq 0$, uncontaminated; $0 < I_{\text{geo}} \leq 1$, uncontaminated to moderately contaminated; $1 < I_{\text{geo}} \leq 2$, moderately contaminated; $2 < I_{\text{geo}} \leq 3$, moderately to heavily contaminated; $3 < I_{\text{geo}} \leq 4$, heavily contaminated; $4 < I_{\text{geo}} \leq 5$, heavily to extremely contaminated; $I_{\text{geo}} > 5$, extremely contaminated.

3.2.2. Potential Ecological Risk Index

The potential ecological risk index was proposed by Swedish scientist Lars Hakanson [31]. It combines the content, properties, and environmental behavior characteristics of soils, and comprehensively considers the synergy of multiple elements. It is calculated as follows:

$$RI = \sum_{i=1}^{n} E_r^i = \sum_{i=1}^{n} T_r^i \times C_f^i = \sum_{i=1}^{n} T_r^i \frac{C_s^i}{C_n^i} \tag{2}$$

where E_r^i is the one-factor pollution index; T_r^i is the toxic response coefficient of the individual pollutant (Zn = 1, Cr/Mn = 2, Cu/Ni/Pb = 5, As = 10, Cd = 30, Hg = 40); C_f^i is the pollution index of a certain metal; C_s^i is the measured value of a heavy metal in the soil; and C_n^i is the reference value of a heavy metal. In this study, the background value of soil heavy metals in Mashan County was used as the reference value. *RI* is the total potential ecological risk index. The grading criteria for E_r^i and *RI* are shown in Table 1.

Table 1. Hakanson potential ecological hazard assessment index.

Index	Potential Ecological Risk Level				
	Low	**Medium**	**Raised**	**High**	**Extremely High**
E_r^i	<40	40~80	80~160	160~320	≥320
RI	<150	150~300	300~600	600~1200	≥1200

3.3. Data Analysis

The data analysis for the heavy metal content in the soil of the study area (maximum, minimum, mean, standard deviation, coefficient of variation) and Pearson's correlation analysis were performed using the software packages Excel 2010 (Microsoft, Redmond, WA, USA), Origin 2018 (OriginLab, Northampton, MA, USA), and SPSS 25 (IBM, New York, NY, USA), and ArcGIS 10.2 (ESRI, RedLands, CA, USA)was used for geostatistical analysis.

4. Results and Discussion

4.1. Soil Heavy Metal Content and Distribution Characteristics

Statistical analysis showed that the mean contents of heavy metals As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in the topsoil of the karst area were 42.1, 9.32, 372, 44.3, 0.259, 76.1, 66.2, and 306 mg/kg (Table 2), respectively, which exceeded the background values of the elements in Mashan County [44] and the background value of soil (layer A) in China [45] (Figure 2). The mean contents of the heavy metals in the topsoil of the non-karst area were 14.6, 0.25, 96, 35.3, 0.098, 18.2, 25.5, and 63 mg/kg, respectively (Table 2). Compared with the karst area, the average heavy metal content in the non-karst area did not exceed the background value of each element in Mashan County, except for As, Cd, Cr, Cu, and Hg; these also exceeded the national soil background value, while the other elements did not (Figure 2). According to the data presented by Wedepohl (1995), the contents of eight elements in the karst area are all higher than abundance value of upper crust [46], indicating that the soil elements in karst area have been significantly enriched during the soil-forming process. In the non-karst area, the contents of Cr, Ni, and Zn are lower than those in the upper crust, while the contents of other elements are higher than those in the upper crust. In the karst area, the content of various elements was significantly higher than in the non-karst area, especially for Cd, the average level of which was 36.9 times that in the non-karst area. The minimum values of As and Cd in karst area both exceeded the background values of Mashan County, with average levels of 1.93 and 21.41 times the background values, respectively, while the average levels of Cr, Cu, Hg, Ni, Pb, and Zn were 1.69, 1.21, 1.65, 1.98, 1.69, and 2.34 times the background values of Mashan County, respectively. According to the Soil Environmental Quality: Risk Control Standard for Soil Contamination of Agricultural Land (GB 15618-2018) [47], there were some samples exceeding the risk screening values of soil As, Cd, Cr, Ni, and Zn in the karst area; the proportions of samples exceeding the standard were 100% (Cd), 90.6% (As), 84.4% (Cr), 68.8% (Zn), and 37.5% (Ni), of which 90.6% of the sample Cd exceeded the risk control value. A quarter of samples in non-karst area had Cd contents exceeding the risk screening value, and there were no samples over risk intervent values. The analysis showed that the average level of heavy metal elements in the soil of the karst area was much higher than that of in the non-karst area (Figure 2). The pH values in the soils of karst and non-karst areas ranged from 7.95 to 5.44 and 6.06 to 4.14, respectively, with mean values of 6.72 and 4.67, respectively, which indicated that the non-karst soils were more acidic than the karst. Since the parent material of the karst area mainly comprised carbonate rock, and the weathering of carbonate rock produces calcium ions that increase the soil pH, the overall level of pH was higher than that of non-karst areas. The average organic matter contents of the soils of the two areas showed that the karst area (23.8 g/kg) contained slightly less organic matter than the non-karst area (25.8 g/kg), with ranges of 12.1–34.8 g/kg and 15.4–38.0 g/kg, respectively.

Table 2. Characteristics of heavy metal content in surface soil of study area.

		Elements (mg/kg)								pH	Corg (g/kg)
		As	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**		
Karst area	Max.	65.7	25.7	758	86.5	0.33	113	103	491	7.95	34.8
	Min.	24.4	1.95	183	20.9	0.14	28.4	37.5	104	5.44	12.1
	Mean	42.1	9.32	372	44.3	0.26	76.1	66.2	306	6.72	23.8
	CV	0.25	0.58	0.34	0.30	0.17	0.31	0.24	0.38	0.11	0.26
Non-karst area	Max.	27.7	0.95	225	73.9	0.24	40.0	37.3	124	6.06	25.8
	Min.	6.21	0.07	33.2	8.60	0.05	8.77	13.6	33.4	4.14	15.4
	Mean	14.6	0.25	95.5	35.3	0.10	18.2	25.5	63.0	4.67	38.0
	CV	0.42	0.80	0.42	0.47	0.34	0.34	0.22	0.33	0.10	0.22
Background value of soil in Masan County [44]		22.2	2.38	140	40.1	0.2	60.4	44.4	199	/	/
Background value of soil (layer A) in China [45]		11.2	0.10	61.2	22.6	0.07	26.9	26.0	74.2	6.70	/
Abundance Value of Upper Crust [46]		1.7	0.1	126	25	0.04	56	14.8	65	/	/

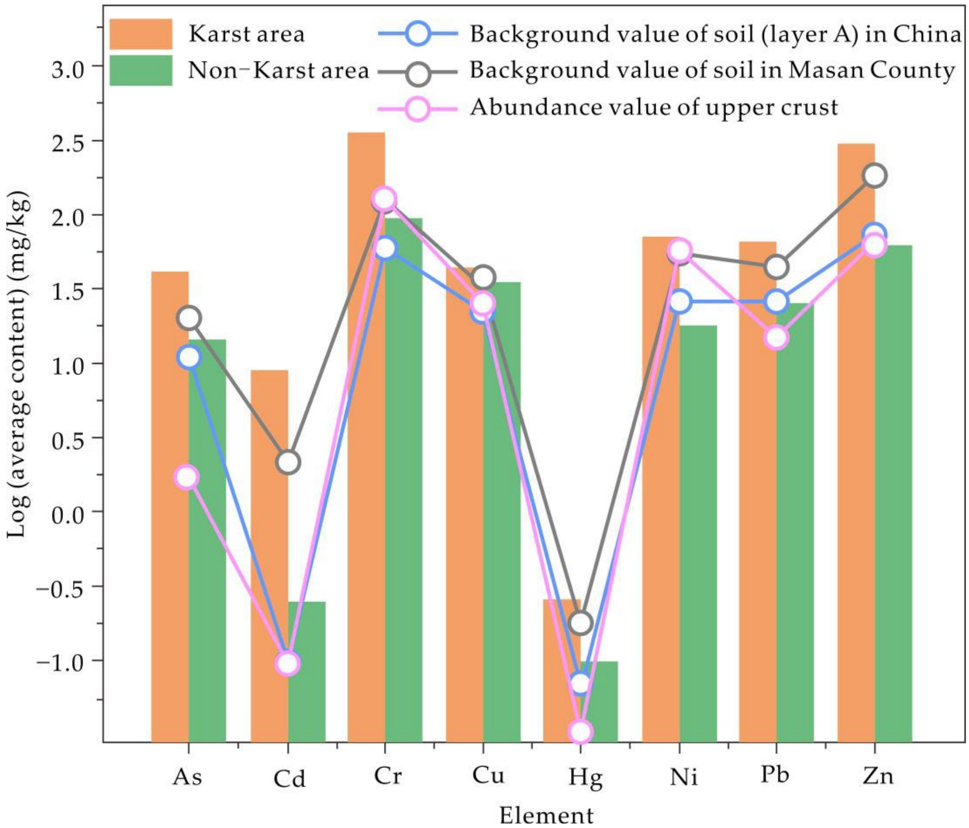

Figure 2. Comparison of soil heavy metal content between karst and non-karst areas.

The variability and uniformity of elements in soil can be reflected by the coefficient of variation (CV) [48–50]. We found moderate variations in As, Cr, Cu, Cu, Hg, Ni, and Pb in karst areas, with high variation in Cd and Zn, then moderate variation in Hg, Ni, Pb, and Zn in non-karst areas, with high variation in As, Cd, Cr, and Cu. The contents and CV of heavy metal elements were combined to reveal the anomalies in the elements and indicate the unevenness of the spatial distribution of heavy metals in the soil in the study area, which may have been affected by the parent materials. Elemental enrichment during migration may also lead to an uneven distribution [13,14]. The CV of elements in non-karst areas was higher than that of karst areas; the anomalies elements of samples were mainly distributed in depressions, which may be affected by the topography. Elemental migration to low-altitude areas or exogenous inputs such as fertilization may have resulted in the dotted high-value areas noted among the overall study area [44].

4.2. Correlation of Soil Heavy Metals and Physicochemical Property

The relationship between elements indirectly reflects whether the elements have the same source; the higher the correlation between the elements, the more likely they are to have the same source [51,52]. Pearson's correlation coefficient analysis of eight heavy metal elements (As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn) from the survey area (Tables 3 and 4) showed that there was a very significant positive correlation between most of the heavy metals in the soil of the karst area; for example, As and Cd, along with Cu, Ni, Pb, and Zn, were significantly correlated at the 0.01 level, and Hg at the 0.05 level, indicating that these elements have strong spatial correlation and similar migration characteristics and homology within karst areas [53]. Cr is mainly significantly related to Cu and As, while it is weakly related to other elements. In the soil of the non-karst area, there was a significant positive correlation between As, Cr, and Hg ($p < 0.01$); Cu, Ni, Pb, and Zn were significantly correlated; Cu, Zn, and other elements were significantly correlated; and Cd was mainly related to Ni and Zn. Overall, multiple groups of heavy metal elements showed a strong correlation between elements in the non-karst area, indicating multi-channel sources. On the basis of correlation analysis, the between-groups linkage was applied for systematic clustering analysis (Figure 3), and by judging the intergroup distance in the spectral graph, the combined characteristics of As-Cd-Cu-Cu-Hg-Ni-Pb-Zn and Cr were determined in the karst area, indicating that the probability of elements in the combination having the same source was high. The combined characteristics of Ni-Cu-Pb-Zn, As-Cr-Hg, and Cd were also shown in the non-karst area.

Table 3. Pearson's correlation analysis of heavy metal elements and basic physical and chemical properties of soil in the karst area.

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
As	1							
Cd	0.47 *	1						
Cr	0.11	−0.12	1					
Cu	0.54 **	0.28	0.46 **	1				
Hg	0.37 *	0.30	0.09	0.48 **	1			
Ni	0.59 **	0.49 **	0.25	0.73 **	0.65 **	1		
Pb	0.63 **	0.74 **	0.18	0.52 **	0.42 *	0.51 **	1	
Zn	0.68 **	0.76 **	−0.15	0.43 *	0.61 **	0.74 **	0.80 **	1
pH	0.13	0.26	0.38 *	0.27	0.28	0.48 **	0.05	0.19
Corg	0.18	0.19	0.26	0.47 **	0.35	0.46 **	0.07	0.24

Note: * and ** represent significant ($p < 0.05$) and extremely significant ($p < 0.01$) correlation, respectively.

Table 4. Pearson's correlation analysis of heavy metal elements and basic physical and chemical properties of soil in the non-karst area.

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
As	1							
Cd	0.44 **	1						
Cr	0.80 **	0.25	1					
Cu	−0.46 **	−0.04	−0.45 **	1				
Hg	0.68 **	0.31	0.77 **	−0.32 *	1			
Ni	−0.18	0.34 *	−0.20	0.64 **	−0.02	1		
Pb	−0.33 *	0.13	−0.57 **	0.52 **	−0.16	0.62 **	1	
Zn	−0.16	0.47 **	−0.20	0.39 *	0.03	0.81 **	0.63 **	1
pH	−0.10	0.07	−0.08	0.09	0.25	0.51 **	0.50 **	0.52 **
Corg	−0.49 **	−0.14	−0.45 **	0.14	−0.26	0.07	0.39 *	0.13

Note: * and ** represent significant ($p < 0.05$) and extremely significant ($p < 0.01$) correlation, respectively.

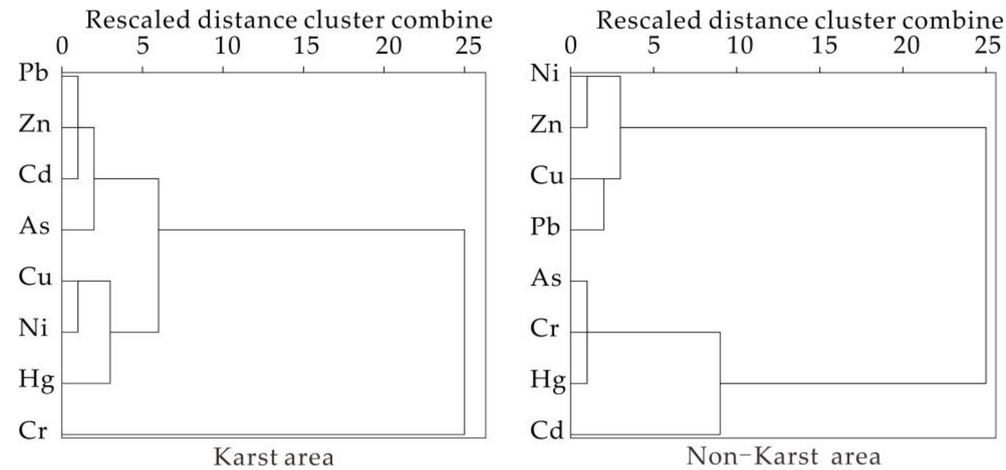

Figure 3. Cluster analysis of soil heavy metals in the study area.

Since there are only a small number of grain deep-processing plants (sugar and alcohol) in the study area, there are no reports of heavy metals exceeding the standard in the atmospheric deposition of the county. Therefore, the heavy metals in this area mainly come from the enrichment of parent materials and agricultural activities. Inappropriate fertilizers and pesticides may also cause heavy metal pollution to the soil [54]. In the karst area of the study area, the soil mainly comprised the carbonate matrix and its residue matrix. Studies have shown that the enrichment of Cd in soils where carbonate rocks develop is mainly related to the adsorption of organic matter, ferromanganese oxides and hydroxides, and clay [55,56]. However, the low correlation of Cd with organic matter and pH in this study indicated that Cd mainly combined with ferromanganese oxides and carbonates [10], and elements such as Cu, Ni, Hg, Pb, Zn, and Cr were mainly related to clay adsorption, competing with Cd for adsorption. Relevant studies have shown that as lattice substitution in carbonate rocks enters the Ca and Mg lattices [25], enrichment occurs with the loss of soluble components such as calcium carbonate and adsorption of iron oxides and clay minerals during weathering. However, there were large differences in the sources of the matrix in the non-karst area. We found a laterite matrix and bedrock residues in the non-karst area, and studies have shown that the bedrock contains plentiful Ni, Cu, and Zn elements, which are released into the soil in the epigenetic environment [57,58]. As, Cr, and Hg have strong combinatorial relationships in non-karst areas and may be related to the sand shale matrix [59,60]. The results also showed that the As and Cr contents were affected by the soil organic matter, and relevant studies have shown that the influence of organic matter on the migration of elements in the soil is very complex [61,62]. In addition to improving the fixation and accumulation of heavy metals in the soil, organic matter may also improve the bioavailability of the elements [62], thereby increasing the migration or plant uptake, showing a negative correlation. Li (2018) reported the enrichment of Cd in soils developed in the limestone, sand shale, and Quaternary laterite matrix in Guangxi (mean contents of 3.45, 2.40, and 0.69 mg/kg, respectively) [63], and our study showed that the Cd content was not significantly affected by soil factors such as pH or organic matter; instead, Cd content may be attributed to the mixed influences of the sand shale and laterite on the matrix.

4.3. Evaluation of Heavy Metal Pollution in Soil

Tables 5 and 6 show the evaluation results of the heavy metal I_{geo} of the topsoil in the karst and non-karst areas. From Table 5, it can be seen that the order of the mean I_{geo} in the karst area was Cd > Cr > As > Pb > Zn > Hg > Ni > Cu. The soil Cd pollution in the karst area was relatively serious; the percentage of medium to heavy pollution, medium pollution, and light pollution levels accounted for 18.75, 43.75, and 25% of the total number of samples, respectively, while the proportion of non-polluted samples was 12.5%. Ni, As, Hg, Pb, Cr, Zn, and Cu were mainly light polluters, with the proportions of 31.25, 81.25, 12.5, 53.13, 75, 56.25, and 10.34%, respectively. The proportion of pollution with Cr was 21.88%. In addition to two samples of Cr and three samples of Cu in the non-karst area, the I_{geo} of the heavy metal elements As, Cr, Hg, Ni, Pb, and Zn was generally pollution-free. In contrast, the pollution level and risk of heavy metal in karst areas was significantly higher than that of in non-karst areas. Due to the large difference in heavy metal content, a small contribution of karst areas to non-karst areas may have caused heavy metals in non-karst areas to exceed the heavy metals in the soil, indicating that it is necessary to focus on prevention and control.

Table 5. I_{geo} classification statistics for heavy metals in surface soil of karst area.

Heavy Metals	Average	Number of Graded Samples						
		$I_{geo} \leq 0$	$0 < I_{geo} \leq 1$	$1 < I_{geo} \leq 2$	$2 < I_{geo} \leq 3$	$3 < I_{geo} \leq 4$	$4 < I_{geo} \leq 5$	$I_{geo} > 5$
As	0.30	6	26	0	0	0	0	0
Cd	1.15	4	8	14	6	0	0	0
Cr	0.76	1	24	7	0	0	0	0
Cu	−0.51	29	3	0	0	0	0	0
Hg	−0.24	28	4	0	0	0	0	0
Ni	−0.34	22	10	0	0	0	0	0
Pb	−0.05	15	17	0	0	0	0	0
Zn	−0.08	14	18	0	0	0	0	0

Table 6. I_{geo} classification statistics for heavy metals in surface soil of non-karst area.

Heavy Metals	Average	Number of Graded Samples						
		$I_{geo} \leq 0$	$0 < I_{geo} \leq 1$	$1 < I_{geo} \leq 2$	$2 < I_{geo} \leq 3$	$3 < I_{geo} \leq 4$	$4 < I_{geo} \leq 5$	$I_{geo} > 5$
As	−1.28	40	0	0	0	0	0	0
Cd	−1.68	40	0	0	0	0	0	0
Cr	−1.86	38	2	0	0	0	0	0
Cu	−0.83	37	3	0	0	0	0	0
Hg	−1.34	40	0	0	0	0	0	0
Ni	−1.75	40	0	0	0	0	0	0
Pb	−1.23	40	0	0	0	0	0	0
Zn	−1.70	40	0	0	0	0	0	0

4.4. Assessment of Potential Ecological Risks of Heavy Metals in Soils

The evaluation results of the potential ecological risk level of soil heavy metals in the karst area are shown in Table 7, with Cd as the main risk element in the area. Its single pollution index ranged from 24.89 to 328.09, and the proportions of low, medium, raised, high, and extreme high ecological risk were 9.38, 25, 43.75, 18.75, and 3.13%, respectively. The Hg single pollution index ranged from 36.2 to 84.56, and 90.63% of the samples showed medium risk. The rest of the elements posed low risks. Other heavy metal elements (As, Cr, Cu, Ni, Pb, and Zn) all showed less than 40 indices of single-factor potential ecological risk, which indicates a slight ecological risk. In contrast, all samples of As, Cr, Cu, Ni, Pb, and Zn from non-karst areas were at a slight ecological risk (Table 8). Meanwhile, three and one samples of Cd and Hg, respectively, presented moderate ecological risks, accounting for 7.5 and 2.5% of the total sample size, respectively, with no strong ecological risks. In summary, Cd and Hg were the main ecologically hazardous heavy metal elements in the soil of karst and non-karst areas, and the potential ecological risk level of karst areas was much higher than that of non-karst areas.

The heavy metals composite potential risk index (*RI*) increased with the increase in the degree of heavy metal pollution in the topsoil. The comprehensive potential risk index of heavy metals in the surface soil of the karst area ranged from 108.01 to 436.74 (Table 7) in the karst area, and there were slight to strong ecological risks, mainly medium risks, accounting for 59.38%, while the proportions of slight and strong risks were 21.88 and 18.75%, respectively. The range of *RI* in non-karst areas was 26.09 to 72.01, presenting a slight ecological risk. Related studies have shown that topographic landforms may play a role in terms of barriers and thus affect the spatial distribution of heavy metals [64–66]. The effects of elevation and slope on the *RI* in this study area can be expressed as $RI = 0.1739 \times \text{elevation} + 81.91$ ($R^2 = 0.0047$) and $RI = 2.1286 \times \text{slope} + 90.223$ ($R^2 = 0.0758$), respectively. The results show that elevation and slope did not cause a significant increase or decrease in *RI*, so topography and geomorphology were not the main influencing factors.

In summary, the higher ecological risk was mainly distributed in the western karst area, indicating that there are more heavy metals in the soil where the carbonate soil matrix is developed.

Table 7. Classification statistics of potential ecological risk index of heavy metals in the soil of the karst area.

Index		Range	Number of Graded Samples				
			Low	Medium	Raised	High	Extremely High
E^i_r	As	11.02~29.66	32	0	0	0	0
	Cd	24.89~328.09	3	8	14	6	1
	Cr	2.64~10.39	32	0	0	0	0
	Cu	2.61~10.80	32	0	0	0	0
	Hg	28.60~66.80	3	29	0	0	0
	Ni	2.35~9.35	32	0	0	0	0
	Pb	4.22~10.60	32	0	0	0	0
	Zn	0.53~2.48	32	0	0	0	0
RI		108.01~436.74	7	19	6	0	0

Table 8. Classification statistics of potential ecological risk index of heavy metals in the soil of the non-karst area.

Index		Range	Number of Graded Samples				
			Low	Medium	Raised	High	Extremely High
E^i_r	As	2.80~12.51	40	0	0	0	0
	Cd	0.86~12.13	40	3	0	0	0
	Cr	0.48~3.25	40	0	0	0	0
	Cu	1.07~9.23	40	0	0	0	0
	Hg	10.62~47.00	39	1	0	0	0
	Ni	0.73~3.31	40	0	0	0	0
	Pb	1.53~4.20	40	0	0	0	0
	Zn	0.17~0.63	40	0	0	0	0
RI		26.09~72.01	40	0	0	0	0

5. Conclusions

The heavy metal element contents in samples of surface soil from the karst area investigated in this study exceeded the background values for Mashan County, the background value of soil (layer A) in China, and the abundance value of the upper crust; Cd levels were the most significant. The contents of eight heavy metals in the non-karst area of the study did not exceed the background values for Mashan County, and the elements besides As, Cd, Cr, Cu, and Hg did not exceed the background national soil values. According to GB 15618-2018, the high-risk samples in karst areas contained Cd (100%) > As (90.6%) > Cr (84.4%) > Zn (68.8%) > Ni (37.5%), and only Cd (25%) in non-karst areas. The degree of variation of each element in the study area was above moderate, indicating the unevenness of the spatial distribution of heavy metals in the soil of the study area, and there were significant differences in the heavy metal contents of the karst and non-karst areas.

The correlation and cluster analyses showed that the karst area was characterized by As-Cd-Cu-Hg-Ni-Pb-Zn and Cr, which were mainly affected by the carbonate parent materials, while the non-karst area was characterized by Ni-Cu-Pb-Zn, As-Cr-Hg, and Cd, which were affected by the mixture of the matrix (with laterite, sand shale, and residue), and to a certain extent, by the migration of elements due to soil erosion or anthropogenic activities.

The average I_{geo} in karst areas descended in the order of Cd > Cr > As > Pb > Zn > Hg > Ni > Cu. Except for the samples in the presence of medium pollution and above in Cd and Cr, the remaining elements were generally at the level of no to light pollution in the non-karst area. However, the pollution level of Cd was relatively serious. In the non-karst area, except for a small number of samples of Cd and Cu, other elements were at the level of pollution-free, but due to the contribution of the karst area, the pollution level of the non-karst area may have been elevated. Between the non-karst areas, the soil was found to be acidic; its potential to cause harm needs to be further studied.

The analysis of the potential ecological risk index of heavy metals in the soil of the study area showed that Cd and Hg were the main ecologically hazardous heavy metal elements in the karst and non-karst areas. The potential ecological risk level of the karst area was much higher than that of the non-karst area, especially for Cd. There were slight to strong ecological risks in the potential risk index of surface soils in karst areas, mainly medium risks, showing as minor ecological risks in non-karst areas. In addition, this study has shown that elevation and slope have little effect on potential ecological risks; instead, the ecological risks are mainly affected by the carbonate soil matrix.

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References

1. US EPA, Office of Solid Waste Emergency Response, Waste Cleanup Risk Assessment. *Risk Assessment Guidance for Superfund (RAGS), Volume I: Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment) Interim*; US EPA: Washington, DC, USA, 2009.
2. Wang, Y. *Elemental Chemistry of Soil Environment*; China Environmental Press: Beijing, China, 1995; p. 394. (In Chinese)
3. Galitskaya, I.V.; Mohan, K.R.; Krishna, A.K.; Batrak, G.I.; Eremina, O.N.; Putilina, V.S.; Yuganova, T.I. Assessment of soil and Groundwater Contamination by Heavy Metals and Metalloids in Russian and Indian Megacities. *Procedia Earth Planet. Sci.* **2017**, *17*, 674–677. [CrossRef]
4. Zhu, S.; Shen, Z.L.; Wang, Y.; Wu, H.R.; Xin, J. Spatial distribution characteristics of heavy metals in the soil-groundwater system around an integrated waste management facility. *China Environ. Sci.* **2021**, *41*, 4320–4332. (In Chinese)
5. Xie, X.J. *Geochemical Atlas of China*; Geology Press: Beijing, China, 2012.
6. Li, M.; Xi, X.H.; Xiao, G.Y.; Cheng, H.X.; Yang, Z.F.; Zhou, G.H.; Ye, J.Y.; Li, Z. National multi-purpose regional geochemical survey in China. *J. Geochme. Explor.* **2014**, *139*, 21–30. [CrossRef]
7. Cheng, H.X.; Peng, M.; Zhao, C.D.; Han, W.; Wang, H.Y.; Wang, Q.L.; Yang, F.; Zhang, F.G.; Wang, C.W.; Liu, F.; et al. Epigenetic geochemical dynamics and driving mechanisms of distribution patterns of chemical elements in soil, Southwest China. *Earth Sci. Front.* **2019**, *26*, 159–191. (In Chinese)
8. Xia, X.Q.; Gong, Q.J.; Xu, C.Y. Research Progresses on Applied Geochemistry from 2011 to 2020 in China: Eco-geochemistry. *Geoscience* **2020**, *34*, 883–896. (In Chinese)
9. Wen, Y.B.; Li, W.; Yang, Z.F.; Zhang, Q.Z.; Ji, J.F. Enrichment and source identification of Cd and other heavy metals in soils with high geochemical background in the karst region, Southwestern China. *Chemosphere* **2020**, *245*, 125620. [CrossRef] [PubMed]
10. Quezada-Hinojosa, R.P.; Matera, V.; Adatte, T.; Rambeau, C.; Föllmi, K.B. Cadmium distribution in soils covering Jurassic oolitic limestone with high Cd contents in the Swiss Jura. *Geoderma* **2009**, *150*, 287–301. [CrossRef]
11. Xia, X.Q.; Ji, J.F.; Yang, Z.F.; Han, H.J.; Huang, C.L.; Li, Y.; Zhang, W. Cadmium risk in the soil-plant system caused by weathering of carbonate bedrock. *Chemosphere* **2020**, *254*, 126799. [CrossRef]
12. Rambeau, C. Cadmium Anomalies in Jurassic Carbonates (Bajocian, Oxfordian) in Western and Southern Europe. Ph.D. Thesis, University of Strasbourg, Strasbourg, France, 2006.
13. Feng, Z.G.; Liu, W.; Zhang, L.Y.; Li, P.S.; Ma, Q. Enrichment and supernormal enrichment phenomenon of Cd in soils developed on Cd-poor carbonate rocks: A case study of karst areas in Guizhou, China. *Geol. Bull. China* **2022**, *41*, 533–544. (In Chinese)

14. Guo, C.; Wen, Y.B.; Yang, Z.F.; Li, W.; Guan, D.X.; Ji, J.F. Factors controlling the bioavailability of soil cadmium in typical karst areas with high geogenic background. *J. Nanjing Univ.* **2019**, *55*, 678–687. (In Chinese)
15. Zheng, M.J.; Zhang, S.; Zhang, M.K. Distribution and heavy metal pollution characteristics of geologically high background farmland in Zhejiang Province. *J. Zhejiang Agric. Sci.* **2022**, *63*, 166–169. (In Chinese)
16. Zhang, L.; McKinley, J.; Cooper, M.; Han, W.; Liu, F.; Song, Y.T.; Peng, M.; Liu, X.J.; Yang, W.; Cheng, H.X. Transfer processes of potential toxic elements (PTE) between rock-soil systems and soil risk evaluation in the Baoshan area, Yunnan Province, southwest China. *Appl. Geochem.* **2020**, *121*, 104712. [CrossRef]
17. Tian, H.C.; Xu, Z.G. Cadmium geochemical behavior and Cadmium pollution in southwest China. *Mod. Min.* **2014**, *30*, 134–136. (In Chinese)
18. Li, J.; Zhan, M.G.; Zhong, X.Y.; Wang, X.Y.; Ouyang, X.D.; Zhao, X.J. Distribution and accumulation of heavy metals in soil-crop systems from a typical carbonate rocks area in Guangxi. *Acta Sci. Circumstantiae* **2021**, *41*, 597–606. (In Chinese)
19. Ni, S.Q.; Ju, Y.W.; Hou, Q.L.; Wang, S.J.; Liu, Q.; Wu, Y.D.; Xiao, L.L. Enrichment of heavy metal elements and their adsorption on iron oxides during carbonate rock weathering process. *Prog. Nat. Sci.* **2009**, *19*, 1133–1139. [CrossRef]
20. Zhang, M.; Xie, Y.Q.; Cai, W.T.; Sun, L.; Zhao, E.N. Hidden danger of cadmium in the soil of ecologic system with virtuous circle in the southwest karst area of China. *Jiangsu Agric. Sci.* **2010**, 295–297. (In Chinese)
21. Liu, X.; Gu, Q.B.; Yang, Q.; Yu, T.; Zhang, Q.Z. Distribution and Influencing Factors of Cadmium Geochemical Fractions of Soils at Carbonate Covering Area in Hengxian and Xiangzhou of Guangxi. *Geoscience* **2017**, *31*, 374–385. (In Chinese)
22. Prokop, Z.; Cupr, P.; Zlevorova-Zlamalikova, V.; Dusek, L.; Holoubek, I. Mobility, bioavailability, and toxic effects of cadmium in soil samples. *Environ. Res.* **2003**, *91*, 119–126. [CrossRef]
23. Li, D.Q.; Li, W.Y.; Lu, Q.; Li, Y.T.; Li, N.; Xu, H.J.; Ren, Z.L.; Zhang, Y.L.; Wang, J.J. Cadmium bioavailability well assessed by DGT and factors influencing cadmium accumulation in rice grains from paddy soils of three parent materials. *J. Soil. Sediment.* **2018**, *18*, 2552–2561. [CrossRef]
24. Quezada-Hinojosa, R.; Föllmi, K.B.; Gillet, F.; Matera, F. Cadmium accumulation in six common plant species associated with soils containing high geogenic cadmium concentrations at Le Gurnigel, Swiss Jura Mountains. *Catena* **2015**, *124*, 85–96. [CrossRef]
25. Hartley, W.; Edwards, R.; Lepp, N.W. Arsenic and heavy metal mobility in iron oxide-amended contaminated soils as evaluated by short- and long-term leaching tests. *Eniron. Pollut.* **2004**, *131*, 495–504. [CrossRef] [PubMed]
26. Su, C.T.; Huang, C.H.; Zou, S.Z.; Luo, F.; Yang, Y.; Zhao, G.S.; Yang, M. Transferring features of elements in soil rich in iron-manganese nodules karst area of Litang, Guangxi. *J. South. Agric.* **2017**, *48*, 1594–1599. (In Chinese)
27. Tang, S.Q.; Liu, X.J.; Yang, K.; Guo, F.; Yang, Z.; Ma, H.H.; Liu, F.; Peng, M.; Li, K. Migration, Transformation Characteristics, and Ecological Risk Evaluation of Heavy Metal Fractions in Cultivated Soil Profiles in a Typical Carbonate-Covered Area. *Huan Jing Ke Xue* **2021**, *42*, 3913–3923.
28. Tang, D.D.; Yuan, X.Y.; Wang, Y.M.; Ji, J.F.; Wen, Y.B.; Zhao, W.F. Enrichment characteristics and risk prediction of heavy metals for rice grains growing in paddy soils with a high geological background. *J. Agro. Environ. Sci.* **2018**, *37*, 18–26.
29. Nemerow, N.L. *Scientific Stream Pollution Analysis*; Scripta Book Company: Washington, DC, USA, 1974.
30. Müller, G. Index of geoaccumulation in sediments of the Rhine River. *GeoJournal* **1969**, *2*, 108–118.
31. Hakanson, L. An ecological risk index for aquatic pollution control. A sedimentological approach. *Water Res.* **1980**, *14*, 975–1001. [CrossRef]
32. Liu, J.; Teng, Y.G.; Cui, Y.F.; Wang, J.S. Review in Ecological Risk Assessment Methods for Heavy Metal Polluted Soils. *Adm. Tech. Environ. Monit.* **2007**, *19*, 6–11.
33. Liu, J.Y.; Zhuo, Z.X.; Sun, S.Y.; Ning, X.A.; Zhao, S.Y.; Xie, W.M.; Wang, Y.J.; Zheng, L.; Huang, R.; Li, B. Concentrations of heavy metals in six municipal sludges from Guangzhou and their potential ecological risk assessment for agricultural land use. *Pol. J. Environ. Stud.* **2015**, *24*, 165–174. [CrossRef]
34. Zhao, D.J.; Wang, X.Q. Distribution, sources and potential ecological risk of heavy metals in the floodplain soils of the karst area of Yunnan, Guizhou, Guangxi. *China Environ. Sci.* **2020**, *40*, 1609–1619. (In Chinese)
35. Xia, X.Q.; Yang, Z.F.; Guo, J.J.; Shao, X.; Han, S.S. Lack of Meticulous Scholarship of Some Authors Reflected by a Citation for a Concept. *Chin. Geol. Educ.* **2015**, *24*, 10–21. (In Chinese)
36. Zhang, P.F.; Shao, L.Y. Facies belts and depositional model of late Permian Heshan formation in Heshan, central Guagnxi, Southern China. *Acta Sedmentologica Sin.* **1990**, *17*, 13–21.
37. Hadjira, B.; Wang, X.; Ma, Z.W.; Wu, M.; Yan, J.X. Preliminary Mineralogical and Geochemical Analysis on the Chihsia Formation of Tieqiao Section, Laibin, Guangxi and Their Geological Implications. *Geol. Sci. Technol. Inf.* **2011**, *30*, 15–19.
38. Zhang, C.L.; Yang, H.; Huang, F.; Cao, J.H. Distribution and influencing factors of selenium content in soil in karst areas in Mashan County, Guangxi, China. *Geophys. Geochem. Explor.* **2021**, *45*, 1497–1503. (In Chinese)
39. Ministry of Land and Resources of the People's Republic of China. *Specification of Land Quality Geochemical Assessment*; (DZ/T 0295-2016); Geological Publishing House: Beijing, China, 2016. (In Chinese)
40. Ministry of Land and Resources of the People's Republic of China. *Specification of Multi-Purpose Regional Geochemical Survey (1:250000)*; (DZ/T 0258-2014); Standards Press of China: Beijing, China, 2014. (In Chinese)
41. Muller, G. Die Schwermetallbelastung der sedimenten des Necker und seiner Nebefluse: Eine Bestandsanfnahme. *Chem. Ztg.* **1981**, *105*, 157–164.

42. Förstner, U.; Muller, G. Concentrations of heavy metals and polycyclic aromatic hydrocarbons in river sediments: Geochemical background, man's influence and environmental impact. *GeoJournal* **1981**, *5*, 417–432. [CrossRef]
43. Hussaini, M.; Bajoga, A.D.; Mustapha, M.; Aliyu, U.S. Assessment of Geo-Accumulation Index (Igeo) In Soil Samples of Fika Agrarian Community of Yobe State, Nigeria, Using Mp-Aes Analytical Technique. *Int. J. Sci. Technoledge* **2019**, *7*, 1–7. [CrossRef]
44. Zhang, C.L.; Zou, X.; Yang, H.; Liang, J.H.; Zhu, T.B. Bioaccumulation and risk assessment of potentially toxic elements in soil-rice system in Karst area, Southwest China. *Front. Environ. Sci.* **2022**, *10*, 1–12. [CrossRef]
45. China National Environmental Monitoring Centre. *Background Values of Soil Elements in China*; China Environmental Press: Beijing, China, 1990. (In Chinese)
46. Wedepohl, K.H. The composition of the continental crust. *Geochim. Cosmochim. Acta* **1995**, *59*, 1217–1232. [CrossRef]
47. Ministry of Ecology and Environment of the People's Republic of China. *Soil Environmental Quality: Risk Control Standard for Contamination of Agricultural Land*; (GB15618-2018); China Environmental Science Press: Beijing, China, 2018. (In Chinese)
48. Wilding, L.P. Spatial variability: Its documentation, accomodation and implication to soil survey. In *Soilspatial Variability*; Nielsen, D.R., Bouma, J., Eds.; Pudoc: Wageningen, The Netherlands, 1985; pp. 166–194.
49. Wollenhaupt, N.C.; Mulla, D.J.; Crawford, C.A.G. Soil Sampling and Interpolation Techniques for Mapping Spatial Variability of Soil Properties. *State Site Specif. Manag. Agric.* **1997**, 19–53.
50. Zhang, R.D. *Theory and Application of Spatial Variation*; Science Press: Beijing, China, 2005. (In Chinese)
51. Zhang, S.; Yang, D.; Li, F.; Chen, H.; Bao, Z.; Huang, B.; Zou, D.; Yang, J. Determination of regional soil geochemical baselines for trace metals with principal component regression: A case study in the Jianghan plain, China. *Appl. Geochem.* **2014**, *48*, 193–206. [CrossRef]
52. Wang, Q.L.; Song, Y.T.; Wang, C.W.; Xu, R.T.; Peng, M.; Zhou, Y.L.; Han, W. Source identification and spatial distribution of soil heavy metals in Western Yunnan. *China Environ. Sci.* **2021**, *41*, 3693–3703. (In Chinese)
53. Rodríguez, J.A.; Nanos, N.; Grau, J.M.; Gil, L.; López-Arias, M. Multiscale analysis of heavy metal contents in Spanish agricultural topsoils. *Chemosphere* **2008**, *70*, 1085–1096. [CrossRef] [PubMed]
54. Shehu, I.; Demaku, S.; Morina, M.; Malsiu, A.; Bytyqi, H.; Behrami, A. Heavy Metals in Soil and Vegetables in Anadrinia Region as a Result of the use of Pesticides, Herbicides and Fertilizers. *J. Int. Environ. Appl. Sci.* **2016**, *15*, 191–196.
55. Huynh, T.; Tong, A.R.; Singh, B.; Kennedy, B.J. Cd-Substituted Goethites—A Structural Investigation by Synchrotron X-ray Diffraction. *Clay. Clay Miner.* **2003**, *51*, 397–402. [CrossRef]
56. Norberto, B.V. *Cadmium Speciation and Phyto-Availability in Soils of the Swiss Jura*; Epfl: Lausanne, Switzerland, 1999.
57. Guo, W.H.; Liu, X.B.; Liu, Z.G.; Li, G.F. Pollution and Potential Ecological Risk Evaluation of Heavy Metals in the Sediments around Dongjiang Harbor, Tianjin. *Procedia Environ. Sci.* **2010**, *2*, 729–736. [CrossRef]
58. Rudnick, R.L.; Gao, S. Composition of the Continental Crust. In *Treatise on Geochemistry*, 2nd ed.; Holland, H.D., Turekian, K.K., Eds.; Elsevier: Oxford, UK, 2014; Volume 4, pp. 1–51.
59. He, T.B.; Dong, L.L.; Li, G.Z.; Liu, Y.S.; Shu, Y.G.; Luo, H.B.; Liu, F. Differences of Heavy Metal Contents in Soils Derived from Different Parent Materials/Rocks in Karst Mountain Area. *J. Agro. Environ. Sci.* **2008**, *27*, 188–193.
60. Xiang, L. Characteristics of Heavy Metal Content in Soil with Different Parent Materials—Taking Dongzhi County as an Example. *J. Anhui Agric. Sci.* **2021**, *49*, 76–79. (In Chinese)
61. Yang, Z.F.; Yu, T.; Hou, Q.Y.; Yang, Y.; Fu, Y.R.; Zhao, X.L. Gerchemical characteristics of soil selenium in farmland of Hainan island. *Geoscience* **2012**, *5*, 837–849.
62. Du, M.Y.; Zhao, X.L. Literature review on the relationship between soil organic matter and heavy metal migration and transformation. *Southwest Hortic.* **2016**, *10*, 92–94.
63. Li, D.Q. Effect Mechanisms of Fe and DOM on Cd Lability in High Heavy Metal Background Soil Under Water Regulations. Ph.D. Thesis, South China Agriculture University, Guangzhou, China, 2018. (In Chinese).
64. Du Laing, G.; Rinklebe, J.; Vandecasteele, B.; Meers, E.; Tack, F.M.G. Trace metal behaviour in estuarine and riverine floodplain soils and sediments: A review. *Sci. Total Environ.* **2009**, *407*, 3972–3985. [CrossRef]
65. Mao, Z.L.; Tan, Z.P.; Huang, S.M. Spatial Distribution Characteristics of Heavy Metal Elements Cd and Pb in Soils of the Youjiang River Valley. *Chin. J. Soil Sci.* **2020**, *51*, 709–716. (In Chinese)
66. Shen, H.Y.; An, R.; Shi, H.D.; Li, X.Y.; Zhang, A.D. Heavy Metal Pollution and Influencing Factors of Agricultural Land in a Typical Watershed in Hunan Province. *Res. Environ. Sci.* **2021**, *34*, 715–724. (In Chinese)