

## Article

# Characteristics, Chemical Speciation and Health Risk Assessment of Heavy Metals in Paddy Soil and Rice around an Abandoned High-Arsenic Coal Mine Area, Southwest China

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**Abstract:** The concentrations of the heavy metals Pb, Cd, Cr, Hg, As, Cu and Zn in soil and locally produced grain (rice) were determined in paddy soil and rice around an abandoned high-arsenic coal mine area of Xingren county, southwest China. The health risk assessment was used to assess the multimedia and multipathway health risks of HM exposure in the study area. The results showed that the concentrations of As, Pb and Cd in soil were all higher than the corresponding limits for HMs in China. In terms of the accumulation and transfer capacity, Cd was more likely to transfer from the roots to rice, and its strong mobility may pose potential risks to local residents. The non-carcinogenic risks and carcinogenic risks of HM exposure in different media and exposure pathways were higher in children than adults. The total non-carcinogenic risks and carcinogenic risks in adults and children were higher than the standard limit values because of the HM exposure through ingesting rice husk. Among the exposure pathways evaluated, the contribution of diet was the largest, and As was the most important heavy metal in terms of the non-carcinogenic risk and carcinogenic risk factors. The total non-carcinogenic risks and carcinogenic risks caused by As in dietary crop (rice) accounted for 52% of the total in both adults and children. In order to maintain the health of residents in the study area, it is necessary to strictly strengthen the monitoring of heavy metal pollution in the study area and find effective soil improvement methods to reduce the health risks caused by heavy metal exposure.

**Keywords:** heavy metals; rice; high-arsenic coal mine; Xingren county; health risk assessment



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## 1. Introduction

Mining activities have promoted regional economic development, but also led to serious heavy metal (HM) pollution in farmland soils, and this trend of deterioration has expanded [1]. HMs cannot be degraded in the environment and are easily enriched along the food chain, thereby accumulating in the human body [2]. Once the HM content exceeds the bearing capacity of soil, soil productivity and quality will decline [3]. HMs in the soil are harmful to human beings mainly through three routes, i.e., direct contact, inhalation and intake [4]. In addition, different HM speciation directly affects the toxicity of HMs and their migration and transformation in the environment [4]. Given the harm of HMs to human body, it is necessary to conduct the health risk assessment of the crops and their rhizosphere soils in the surrounding mining areas, as well as the speciation characteristics of HMs in the soil.

Several researchers have conducted some efforts in the health risk assessment of HMs in the crops and their rhizosphere soils [5–7]. Haghazadeh et al. [5] evaluated the

HM pollution in paddy and rice grains in the Zarjoub and Goharroud river basins in northern Iran. The results reported moderate to heavy pollution and moderate toxicity for sediments in the Goharroud River, and moderate pollution and toxicity for sediment of the Zarjoub River. Strangely, rice had an intermediate accumulation ability for Cu, Zn and Mn, and a weak and very weak accumulation ability for Pb/Ni and As/Co/Cr, respectively. Sarkar et al. [6] collected the samples of sediment, water and wild rice in Sand Point sloughs on L'Anse Bay and a nearby inland lake, Lake Plumbago. Arsenic is of the higher bioaccumulation at both locations and the hazard index value for wild rice seeds from both sites was high. Anwarul Hasan [7] examined the level of heavy metals in soil and rice samples in Savar, Gazipur and Ashulia (Bangladesh). The order of heavy metals in the soil and rice samples was  $\text{Fe} > \text{Zn} > \text{Ni} > \text{Cr} > \text{Pb} > \text{Co} > \text{Cu} > \text{Cd} > \text{As}$  and  $\text{Zn} > \text{Cu} > \text{Cr} > \text{Co} > \text{Fe} > \text{Cd} > \text{Pb} > \text{Ni} > \text{As}$ , respectively. The obtained contents of Zn, Cd, Cr and Co exceeded the WHO/FAO recommended maximum tolerance values. The coal mine in Xingren County, southwest Guizhou, southwest China, has a high arsenic content [8]. Long-term mining activities have caused serious environmental pollution around the mining areas in Xingren County, especially for paddy fields. In soils with high contents of HMs, excessive amounts of HMs accumulate in planted vegetables and rice, bringing high health risks to local residents. Currently, relevant departments have conducted several studies on heavy metal pollution in the coal mining area of Xingren County [8–10]. The above-mentioned studies mainly focused on the determination of HM contents in the soil of the coal mining area, but ignored the HM pollution situation of the farmland around the coal mining area, and did not explore the health risks of HMs in the farmland soil and crops. Therefore, comprehensive evaluation methods were urgently used to assess the health risks that HM pollution may pose to local residents in this area.

Currently, there are many evaluation methods used for assessing HM pollution [11–13], among which a health risk assessment and risk assessment code are commonly used to analyze the effect of the total contents and speciation of HMs on the health of local residents, respectively [14]. Karimian et al. [15] evaluated the health and ecological risks of HMs in the soil of a Tehran landfill. This study showed that while the hazard index value of children was 6.5 times higher than that of adults, the values of both landfill workers and residents in the target area were at a safe level. Zhang et al. [16] reported that the contamination of HMs in the Shi River Basin soil in China was slightly to moderately polluted, and the risk assessment results showed that all HMs in the area had higher carcinogenicity and other health risks for children than adults, and oral intake was the main route for these pollutants to enter the body. Fan et al. [17] analyzed the heavy metal pollution status of the soil around the power plant in Jinsha County according to the risk assessment coding method, and the research showed that the effective state of Cd accounted for 18.17%, posing a moderate risk level to the environment, Cr and Zn elements were in a low-risk state, and Hg, Pb, As and Cu were in a risk-free state. Up to now, although many studies have focused on HM pollution in the soil of the coal mining area in Xingren County, none of them involved the surrounding farmland and crops, which will lead to health risks from HMs in the coal mining area for local residents through the food chain. Therefore, this study was aiming to: (1) determine the total contents and their speciation of HMs in a paddy; (2) reveal the relationship between HM contents and physical and chemical indexes in the soil; (3) evaluate the migration and accumulation characteristics of HMs in rice; and (4) investigate the health risks of HMs in the soil and rice grains for local residents.

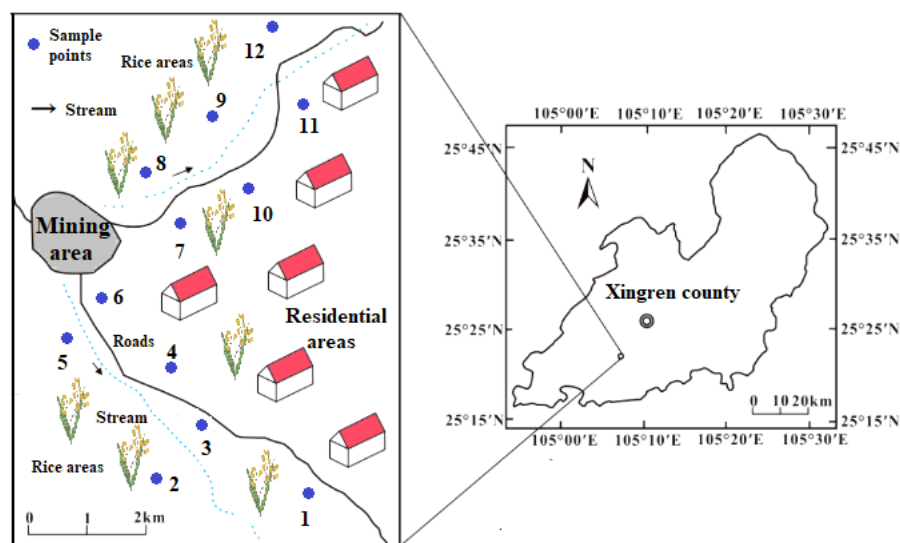
## 2. Materials and Methods

### 2.1. Study Area and Sampling

Xingren County ( $104^{\circ}54' - 105^{\circ}34'$  E and  $25^{\circ}16' - 25^{\circ}48'$  N) is located in the southwest of Guizhou Province, China. It has a subtropical warm and humid monsoon climate, with an annual average temperature of  $15.2^{\circ}\text{C}$ . Most crops in most areas are harvested mainly twice a year, while in some alpine regions they are harvested once a year. The annual precipitation of Xingren County is 1320.5 mm, and the rainy season precipitation

is 1116.3 mm, accounting for 84.5% of the annual precipitation. The unique climate is not only suitable for the development of animal husbandry, but also suitable for the growth of various plants and crops. The highest point in the territory is 2014 m, the lowest altitude is 460 m and the county sits at an elevation of 1350 m. The total land area of Xingren County is 178,500 hectares. The county is rich in mineral resources, mainly including coal, gold, iron, antimony, mercury, uranium, sulfur, etc. With a prospective reserve of more than 4.5 billion t, anthracite was listed as one of China's 200 key coal-producing counties and was recognized as "Xingren Coalfield" by the National Geological Reserves Agency. Most of the mineral resources are still to be explored and developed. Obviously, coal resources have become the main mineral resources in the county [8].

In mid-August 2022, surface soil (12 samples) and corresponding rice plant tissues (roots, stems, leaves and grains) were collected from the rice planting area around the Xingren Coal Mine (Figure 1). The husk of the obtained rice grains were further removed and used to be analyzed. The soil samples were collected by a random sampling method, that is, three times at different locations of each sampling point, and then mixed evenly as the sample of that sampling site. The location of the sampling points was determined by GPS, and the environmental conditions of the sampling points were recorded in detail. All samples were stored in sealed plastic bags and brought back to the laboratory. The soil samples were dried to a constant weight in an oven, grinded in a mortar and all were passed through a 200 mesh nylon sieve for storage and standby. The collected plant samples were dried and screened for standby.



**Figure 1.** The information of sampling points in Xingren county.

## 2.2. Chemical Analysis

Pb, Cr, Cu, Zn, K and Cd in soil were digested by the mixed acid ( $\text{HF}:\text{HClO}_4:\text{HNO}_3 = 2:2:1$ ). Hg and As in the soil were digested by an aqua regia [18]. Cd content was determined by a graphite furnace atomic absorption spectrometer (ZEE nit 700P, Jena, Germany). The Hg and As content were determined by a non-dispersive atomic fluorescence spectrometer (Beijing, Chitian, AFS-933). Other HM contents were determined by an inductively coupled plasma-atomic emission spectrometer (Perkin Elmer Company, Waltham, MA, USA). The pH values of the soil samples were measured by a PHS-3C meter [19] and the nitrogen (N) content was measured by the Kjeldahl method [20]. Soil phosphorus (P) content was determined according to HJ 632–2011 proposed by Environmental Protection Law of the People's Republic of China. Soil organic matter (SOM) was measured according to HJ 615–2011. Each sample was set with three parallel samples. The quality control was carried out using the national soil standard reference material (GSS-24), the error was kept within

5%, the recovery rate was 81% to 109% and the measurement results were within the allowable error range.

The five-step continuous extraction method of Tessier was used to extract the five HM forms of exchangeable (F1), carbonate-bound (F2), iron–manganese oxide (F3), organic-bound (F4) and residual fractions (F5) of HMs [21,22]. Their contents were also determined by ICP-MS. The specific steps of Tessier’s 5-step continuous extraction method are as follows: (1) in the exchangeable state: 2.00 g of soil sample was added to 16 mL of 1 mol/L  $\text{MgCl}_2$  solution with pH = 7.0, shaking at 25 °C for 1 h and centrifuging for 10 min. The supernatant was immediately taken, and deionized water was used to wash the residue. (2). Carbonate-bound fraction: with pH = 5.0, 16 mL of 1 mol/L NaAc solution was added into the above mixtures, shaking at 25 °C for 6 h, and then centrifuged for 10 min. The supernatant was taken and the residue was washed with deionized water. (3) Iron–manganese oxide fraction: 16 mL of 0.04 mol/L  $\text{NH}_2\text{OH}\cdot\text{HCl}$  was added to the above mixtures, shaking at 95 °C for 6 h intermittently, and then centrifuged for 10 min, and the supernatant was subsequently taken and deionized water was used again to wash the residue. (4) Organic-bound fraction: with pH = 2.0, 3 mL of 0.01 mol/L  $\text{HNO}_3$  and 5 mL of 30%  $\text{H}_2\text{O}_2$  were added to the above residues, heating the water bath to 85 °C, and then adding 5 mL of 30%  $\text{H}_2\text{O}_2$  again at pH = 2.0 and heating for another 2 h after intermittent shaking for 2 h, intermittently shaking after cooling to 25 °C. A total of 5 mL of 3.2 mol/L  $\text{NH}_4\text{Ac}$  was added into the mixtures, shaking continuously for 30 min, and then centrifuged for 10 min, taking the supernatant and immediately washing the residue several times with deionized water. (5) Residual fraction: after the first four steps of extraction, the residue was digested by the  $\text{HNO}_3\text{-HCl-H}_2\text{O}_2$  method, and then the contents were determined by ICP-MS.

### 2.3. Ecological Risk of HMs in Soils

#### 2.3.1. Ratios of Secondary Phase and Primary Phase

The HM fractions are closely related to their migration characteristics. Compared with the other four fractions of HMs, the chemical properties of residual fractions are stable and difficult to release into the surrounding environment. Therefore, the distribution ratio of the secondary and primary phase (RSP) has been developed based on the HM fractions [23]. The primary phase in this method refers to the residual state of HMs in the soil, and other forms except the residual state are collectively referred to as the secondary phase. The secondary phase of HMs is smaller than the primary phase, indicating that the possibility of HM existence and transmission in the environment is smaller, and the potential ecological risk to the environment and harm to the human body are also relatively lesser. In this study, the RSP method was used to analyze the ecological risk of HMs in the soil of the study area, and the calculation formula was as follows [23]:

$$\text{RSP} = \frac{M_{\text{sec}}}{M_{\text{prim}}} \quad (1)$$

where  $M_{\text{sec}}$  is the content of HMs in the secondary phase, i.e., the content of the non-residual fraction.  $M_{\text{prim}}$  is the content of HMs in the primary phase, i.e., the content of the residual fraction. According to the value of the RSP, the ecological risk of HMs in the soil can be divided into four levels.  $\text{RSP} < 1$ ,  $1 < \text{RSP} < 2$ ,  $2 < \text{RSP} < 3$  and  $\text{RSP} > 3$  represent no, mild, moderate and severe risks, respectively.

#### 2.3.2. Risk Assessment Code

The bioavailability of different chemical species of HMs in soil is different, which leads to different degrees of harm to the soil. The higher the bioavailability of the HMs, the greater the harm to the soil ecological environment. The risk assessment code (RAC) method fully considers the bioavailability of HMs in the soil, which can better determine

the degree of risk caused by the possible release of HMs into the environment [22]. The calculation formula was as follows [22]:

$$\text{RAC} = \frac{F_1 + F_2}{F_1 + F_2 + F_3 + F_4 + F_5} \quad (2)$$

where RAC represents the ratio of active fractions of HMs to the sum of all HMs' fractions in the soil.  $F_1$ ,  $F_2$ ,  $F_3$ ,  $F_4$ ,  $F_5$  are exchangeable, carbonate-bound, Fe–Mn oxide, organic-bound and residual fractions, respectively.  $\text{RAC} < 1\%$ ,  $1\% < \text{RAC} < 10\%$ ,  $10\% < \text{RAC} < 30\%$ ,  $30\% < \text{RAC} < 50\%$  and  $\text{RAC} > 50\%$  represent no, slight, medium, high and extremely high risks, respectively.

### 2.3.3. Accumulation and Transfer Factors

The accumulation factor (AF) and transfer factor (TF) were used to evaluate the ability of plants to accumulate HMs, which reflects the ability of plants to absorb HMs from the soil and transfer them upwards from the roots after uptake, respectively [24,25]. The calculation formula was as follows [25]:

$$\text{AF} = \frac{w_p}{w_s} \quad (3)$$

$$\text{TF}_{s-r} = \frac{w_s}{w_r} \quad (4)$$

$$\text{TF}_{l-r} = \frac{w_l}{w_r} \quad (5)$$

$$\text{TF}_{g-r} = \frac{w_g}{w_r} \quad (6)$$

where  $w_p$  and  $w_s$  represent the contents of HMs in single rice (the sum of HMs in all tissues) and soil, respectively.  $w_r$ ,  $w_s$ ,  $w_l$  and  $w_g$  represent the concentrations of HMs in the roots, stems, leaves and grains of rice, respectively.

### 2.3.4. Health Risk Assessment

HMs in different media can enter the human body through three exposure routes: ingestion, inhalation and dermal contact, thus bringing carcinogenic and non-carcinogenic health risks [26]. In accordance with the US EPA, Hg, As, Ni, Pb, Cd, Cr, Cu and Zn were treated as non-carcinogenic elements, and As, Cd, Ni and Cr were defined as carcinogenic elements [27,28]. The health risk assessment model includes carcinogenic risk and non-carcinogenic risk [29]. Among them, carcinogenic risk refers to the risk index of carcinogenic diseases and injuries caused by the human exposure to pollutants with pollution effects. The non-carcinogenic risk refers to the harm of the non-carcinogenic risk caused by the human exposure to pollutants with pollution effects. In this study, 3 exposure routes were taken into account: ingestion, inhalation and dermal contact [30]. Non-carcinogenic and carcinogenic risk were calculated using the following equations [31], and all the parameters and values employed in this study are described in Table 1.

$$\text{ADD}_{\text{ing}} (\mu\text{g}/\text{kg}/\text{day}) = \frac{C_w \times \text{IR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \quad (7)$$

$$\text{ADD}_{\text{inh}} (\mu\text{g}/\text{kg}/\text{day}) = \frac{C_w \times \text{InhR} \times \text{EF} \times \text{ED}}{\text{PEF} \times \text{BW} \times \text{AT}} \quad (8)$$

$$\text{ADD}_{\text{derm}} (\mu\text{g}/\text{kg}/\text{day}) = \frac{C_w \times \text{SA} \times \text{CF} \times \text{SL} \times \text{ABS} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \quad (9)$$

$$HQ_i = \sum_{i=1}^3 \frac{ADD_{ij}}{RfD_{ij}} \quad (10)$$

$$HI = \sum_{i=1}^8 HQ_i \quad (11)$$

$$CR_i = \sum_{j=1}^3 ADD_{ij} \times SF_{ij} \quad (12)$$

$$TCR = \sum_{i=1}^4 CR_i \quad (13)$$

where  $ADD_{ing}$ ,  $ADD_{inh}$  and  $ADD_{derm}$  are the average daily exposure of HMs via dietary ingestion, inhalation and dermal contact routes. Table 1 examines the parameters of the health risk assessment of HMs [31]. Generally, the maximum acceptable carcinogenic risk recommended by mainstream institutions is  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-4} a^{-1}$ . Alternatively, one could say that when  $CR_i$  ( $TCR$ )  $< 1 \times 10^{-6}$ , the cancer risk can be ignored. When  $CR_i$  ( $TCR$ )  $> 1 \times 10^{-4}$ , it indicates that there is a large potential carcinogenic risk, and relevant measures must be taken to reduce the risk. When the hazard quotient ( $HQ_i$ ) or  $HI < 1$ , the non-carcinogenic health risk can be ignored. When either value is greater than 1, there is a non-carcinogenic health risk [32].

**Table 1.** Exposure parameters for human health risk assessment [33–37].

| Parameter                  | Description                               | Value   |
|----------------------------|---|---|
| $C_w$                      | HMs concentration (mg/kg)                 | Value from present study  |
| IR (rice)                  | Ingestion rate (g/d)                      | 420 (Adult) and 150 (Children)  |
| IngR (soil)                | Soil ingestion rate(g/d)                  | 0.1 (Adult) and 0.2 (Children)  |
| EF                         | Exposure frequency                        | 365 days/year   |
| ED (noncarcinogenic)       | Exposure duration (a)                     | 30 (Adult) and 6 (Children)   |
| ED (carcinogenic)          | Exposure duration (a)                     | 70 (Adult) and 70 (Children)  |
| BW                         | Body weight (kg)                          | 70 kg (Adult) and 15 kg (Children)  |
| AT (noncarcinogenic)       | Averaging time in years                   | $ED \times 365$ (Adult), $ED \times 365$ (Children)   |
| AT (carcinogenic)          | Averaging time in years                   | 25,550 (Adult and Children)   |
| SA                         | Exposed skin area (cm <sup>2</sup> )      | 5700 (Adult) and 2800 (Children)  |
| PEF                        | Dust emission factor (m <sup>3</sup> /kg) | $1.36 \times 10^9$ (Adult and Children)   |
| CF                         | Unit conversion factor (kg/mg)            | $1 \times 10^{-6}$ (Adult and Children)   |
| SL                         | Adhesion factor (mg/(cm <sup>2</sup> ·d)) | 0.07 (Adult) and 0.02 (Children)  |
| ABS                        | Dermal absorption fraction                | 0.001 (Other metals, adult and children)<br>0.03 (As, adult and children)                   |
| RfD Ingestion (mg/kg/day)  | Reference dose                            | 0.0014 (Pb); Cr (0.003); Cd (0.001); Cu (0.04); Zn (0.3); As (0.0003); Hg (0.0003)          |
| RfD Dermal (mg/kg/day)     | Reference dose                            | 0.0014 (Pb); 0.000075 (Cr); 0.000025 (Cd); 0.04 (Cu); 0.06 (Zn); 0.0003 (As); 0.000024 (Hg) |
| RfD Inhalation (mg/kg/day) | Reference dose                            | 0.0014 (Pb); 0.0000286 (Cr); 0.0000571 (Cd); 0.04 (Cu); 0.3 (Zn); 0.0003 (As); 0.0003 (Hg)  |
| SF Ingestion (mg/kg/day)   | Slope factor                              | 0.501 (Cr), 6.1 (Cd) and 1.5 (As)   |
| SF Dermal (mg/kg/day)      | Slope factor                              | 2.0 (Cr), 24.4 (Cd) and 1.55 (As)   |
| SF Inhalation (mg/kg/day)  | Slope factor                              | 42 (Cr), 6.3 (Cd) and 15.1 (As)   |
| InhR                       | Inhalation rate (m <sup>3</sup> /d)       | 20 (Adult) and 10 (Children)  |

According to the US Environmental Protection Agency's "Guidelines for Site Environmental evaluation in China" (DB11/t656-2009) and existing research results both domestically and internationally, it should be emphasized that the concentration of Cr in this study referred to the total concentration of Cr [31]. In addition, it should be pointed out that there is no reference dose or slope factor for the total Cr in the US EPA so far, only



the reference dose for  $\text{Cr}^{6+}$  and  $\text{Cr}^{3+}$ , as well as the slope factor for  $\text{Cr}^{6+}$ . Available studies pointed out that the majority of Cr in upland soils was in the form of  $\text{Cr}^{6+}$ , which accounted for about 70% of the total Cr. Therefore, the reference dose or slope factor for  $\text{Cr}^{6+}$  will be used in this study to ensure that both the principle of maximum risk and the role of early warning are fully considered [38–40].

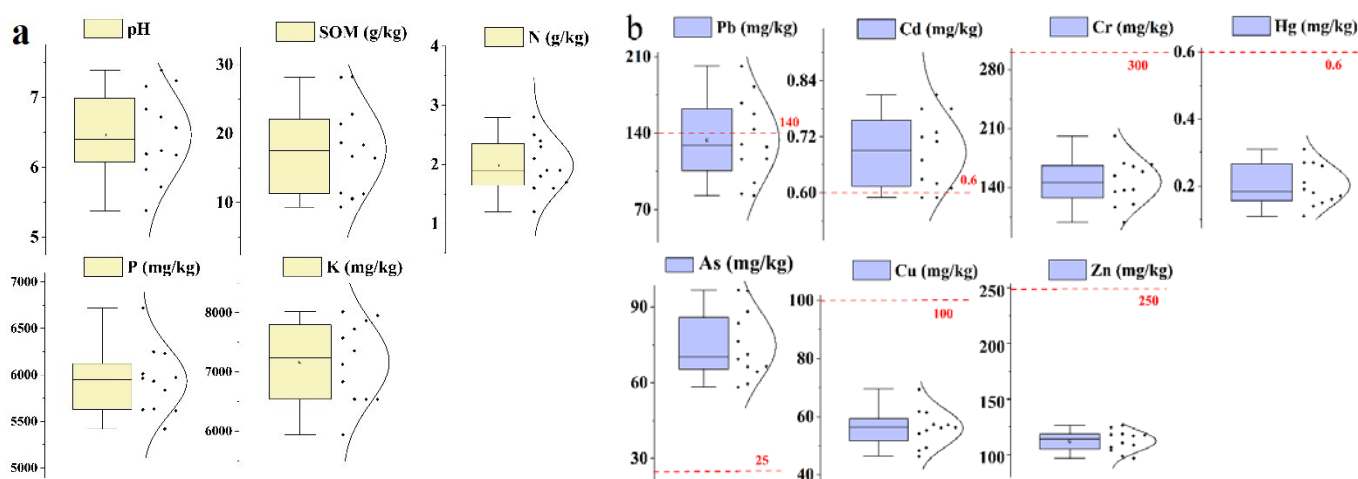
### 2.3.5. Statistical Analysis

ANOVA was used to evaluate the differences in HM concentrations and speciations between different sites. A redundancy analysis was performed to evaluate the relationships between the soil physicochemical parameters and HMs using the “vegan” package of R language 4.2. IBM SPSS 22.0 and Microsoft Excel 2022 were used to process the raw data and perform statistical analyses of the results. The sampling sites were generated using ArcGIS 10.4. All figures were drawn using Origin 2021.

## 3. Results

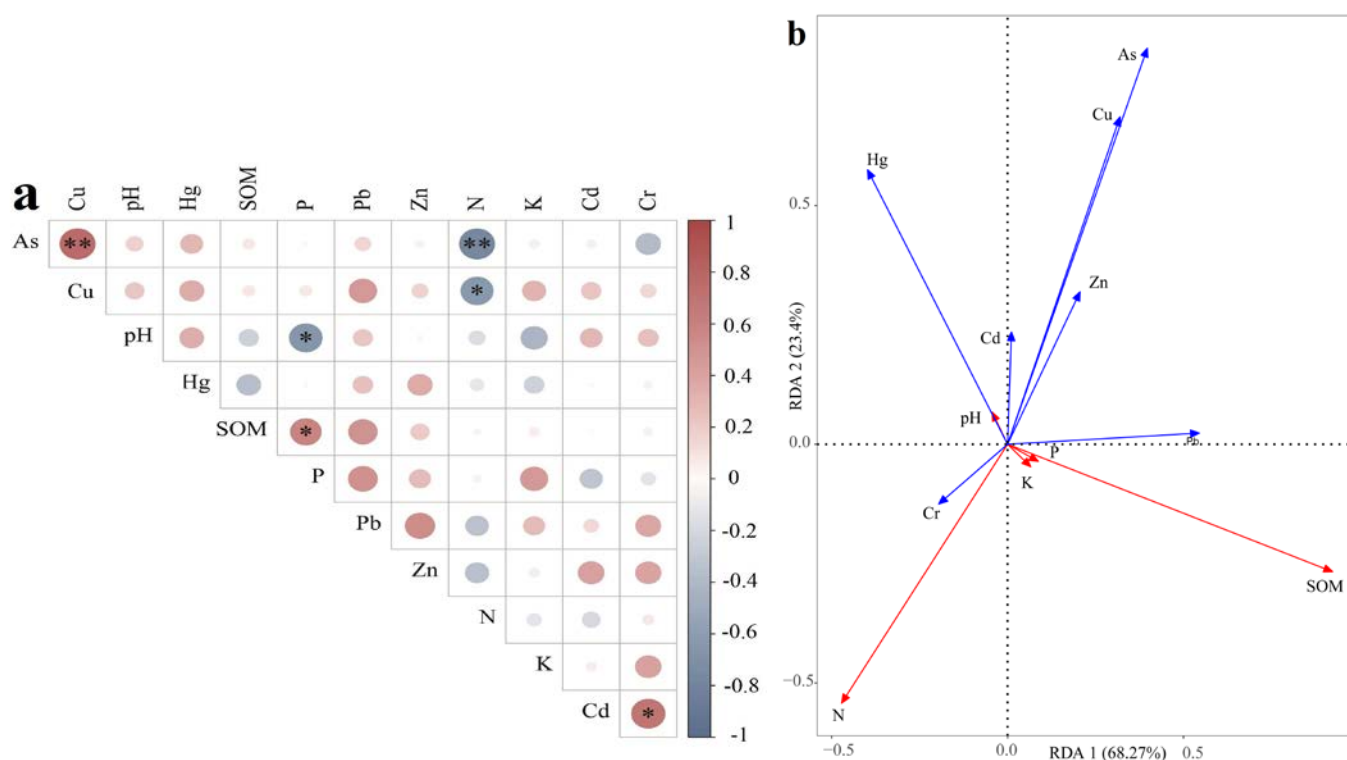
### 3.1. HM Contents and Physicochemical Parameters in Soil and Rice

Figure 2a shows that the pH of the soil was  $6.47 \pm 0.60$  and its coefficient of variation in the total samples was relatively small. The SOM content ranged from 9.35 to 28.19 g/kg, with an average value of 17.77 g/kg, which belonged to the medium-low level according to the classification standards of the Second National Soil Census in China. The nitrogen concentration in the soil samples was  $1.98 \pm 0.42$  g/kg, which was classed as high level. The phosphorus content in the study area was at the medium-low level, ranging from 5.42 to 6.72 mg/kg. The total potassium content in the soil was  $7.17 \pm 0.66$  mg/kg, which was at a relatively low level. In summary, the values of the physical and chemical indicators in the study area were relatively low. Figure 2b shows that the Pb contents ( $133.66 \pm 36.57$  mg/kg) in several soil samples exceeded the limited value (140 mg/kg) according to the soil environmental quality risk control standard for the soil contamination of agricultural land proposed by China (GB 15618-2018). Only the Cd contents in the minor soil samples were greater than the threshold (0.6 mg/kg). The concentrations of Cr, Hg, Cu and Zn in the soil samples were far less than the limited values. The severely excessive As content in the soil of the study area indicated that As was the main pollution factor in the selected HMs and metalloids.



**Figure 2.** Soil physical and chemical parameters (a) and HM (b) contents ( $n = 12$ ;  $6.47 \pm 0.63$  and  $\text{CV}\% = 9.71\%$  for pH;  $17.77 \pm 6.50$  g/kg and  $\text{CV} = 36.60\%$  for SOM;  $1.98 \pm 0.45$  g/kg and  $\text{CV} = 22.83\%$  for N;  $5933.86 \pm 353.81$  mg/kg and  $\text{CV} = 5.96\%$  for P;  $7165.58 \pm 683.93$  mg/kg and  $\text{CV} = 9.55\%$  for K;  $133.66 \pm 38.20$  and  $\text{CV} = 28.57\%$  for Pb;  $0.69 \pm 0.08$  and  $\text{CV} = 11.50\%$  for Cd;  $146.42 \pm 28.11$  and  $\text{CV} = 19.20\%$  for Cr;  $133.66 \pm 38.20$  and  $\text{CV} = 28.57\%$  for Pb;  $0.69 \pm 0.08$  and  $\text{CV} = 11.50\%$  for Cd;  $146.42 \pm 28.11$  and  $\text{CV} = 19.20\%$  for Cr;  $0.20 \pm 0.06$  and  $\text{CV} = 30.92\%$  for Hg;  $74.68 \pm 13.48$  and  $\text{CV} = 18.04\%$  for As;  $56.09 \pm 6.37$  and  $\text{CV} = 11.36\%$  for Cu;  $112.04 \pm 9.64$  and  $\text{CV} = 8.60\%$  for Zn).

The heat map (Pearson correlation) and redundancy analysis were used to reveal the inner relationships between the HMs and physicochemical parameters. Figure 3a demonstrated that the concentration of As in the soil was significantly positively correlated with Cu and negatively correlated with N ( $p < 0.01$ ). This may be attributed to the fact that nitrification is an important biological process of the soil nitrogen cycle, and HM stress can inhibit this process [41]. The Cu content of the soil showed a significant negative correlation ( $p < 0.05$ ) with N, while the P content of the soil showed a significant negative and positive correlation ( $p < 0.05$ ) with the pH and SOM, respectively. The Cd content of the soil was positively correlated with Cr ( $p < 0.05$ ). In addition, the redundancy analysis also revealed a significant negative correlation between the N and As content of the soil (Figure 3b). The N and SOM contents in the soils were closer to HMs and metalloids in comparison to the pH values.



**Figure 3.** The correlation between soil physicochemical parameters and HMs using a heat map (a) and redundancy analysis (b). ( $n = 12$ , “\*” and “\*\*” represent  $p < 0.05$  and  $p < 0.01$ , respectively).

### 3.2. Evaluation of HM Speciation Contents in Soil

Tessier’s extraction method was utilized to analyze the speciations of HMs. The present study revealed that the order of Pb speciation was residual > Fe–Mn-oxide-bound > organic-bound > carbonate-bound > exchangeable fractions (Figure 4). For Cd speciation in the soil, the percentage of the exchangeable fraction increased, implying that Cd may be more easily absorbed by rice. The ratio of the residual fraction in Cr, Hg, As, Cu and Zn speciation was at a maximum. The exchangeable fraction in Cr, Hg, As, Cu and Zn speciation was the lowest, which indicated that they may not be easily absorbed by rice.

The RSP values of Cd, Zn, Hg, Cu and Pb in the soil of the study area were significantly higher than those of other HMs and metalloids, ranging from 4.10–7.28, 2.87–6.25, 1.11–9.29, 0.94–1.64 and 0.91–1.92, respectively (Figure 5a). For Cr and As, the RSP values of all points did not exceed 1, indicating that the ecological risk of these two HMs was relatively slight. According to the average values of the statistical results of the RSP data, the ecological risks of HMs in the soil of the study area were as follows: Cd ( $5.73 \pm 1.00$ ) > Zn ( $4.33 \pm 0.93$ ) > Hg ( $3.11 \pm 2.49$ ) > Cu ( $1.39 \pm 0.20$ ) > Pb ( $1.22 \pm 0.26$ ) > As ( $0.04 \pm 0.00$ ) > Cr ( $0.02 \pm 0.01$ ). Among them, Cd, Zn and Hg



in the soil were classed as being of severe risk, while Cu and Pb were of mild risk. Therefore, it was still necessary to pay attention to the activities of Cd, Zn and Hg in the soil of the study area. The RAC ranges of various HMs in the topsoil of the study area were 0.92% to 32.35% for Pb, 4.10% to 46.79% for Cd, 0.02% to 13.40% for Cr, 1.15% to 17.42% for Hg, 0.04% to 0.87% for As, 0.94% to 29.70% for Cu and 2.87% to 43.14% for Cu (Figure 5b). According to the average values of the RAC data statistical results, the ecological risks of HMs in the soil of the study area were as follows: Cd ( $16.12 \pm 14.86\%$ ) > Zn ( $13.63 \pm 13.87\%$ ) > Cu ( $9.47 \pm 11.56\%$ ) > Pb ( $8.63 \pm 12.78\%$ ) > Hg ( $7.46 \pm 5.74\%$ ) > Cr ( $3.85 \pm 5.46\%$ ) > As ( $0.23 \pm 0.28\%$ ). According to the RAC evaluation criteria, Cd and Zn in the soil were at medium risk, Cu, Pb, Hg and Cr were at slight risk and As in the soil was risk free.

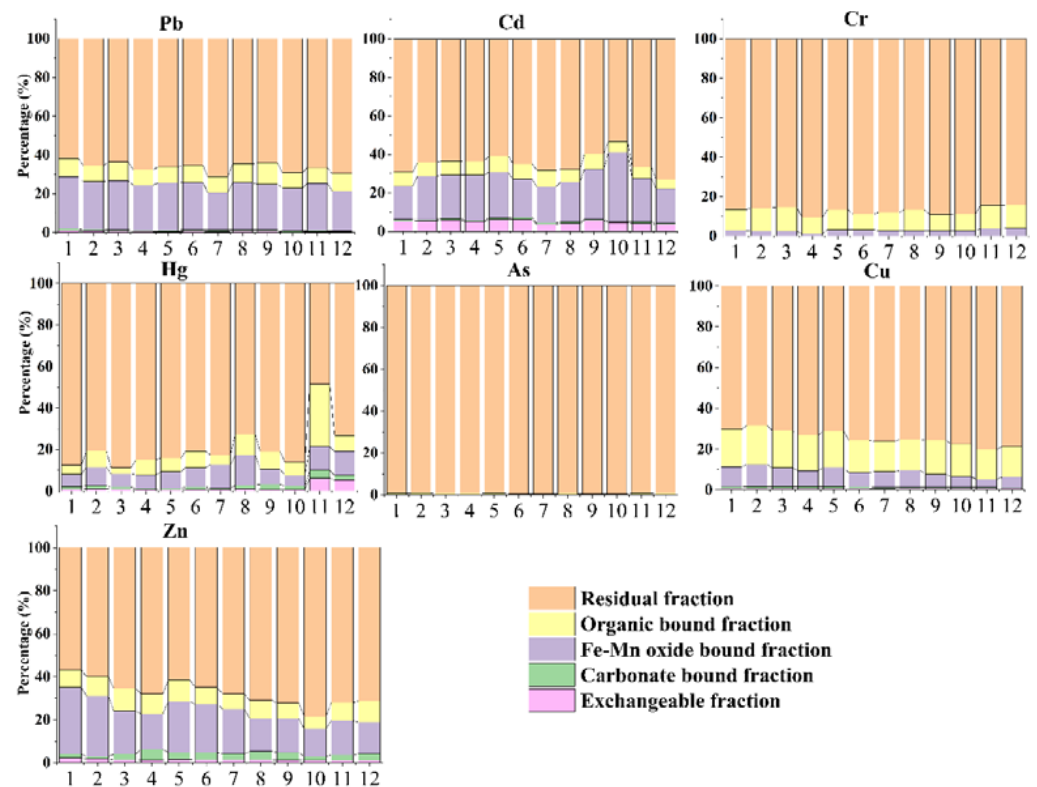


Figure 4. Speciation analysis of HMs in the soil using Tessier's extraction method ( $n = 12$ ).

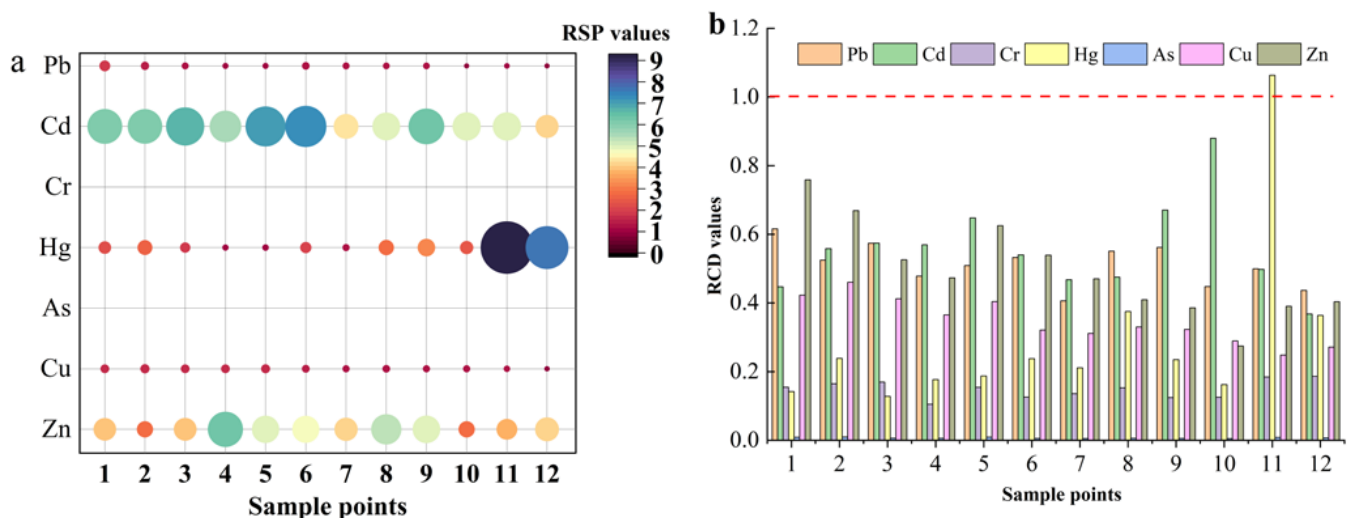
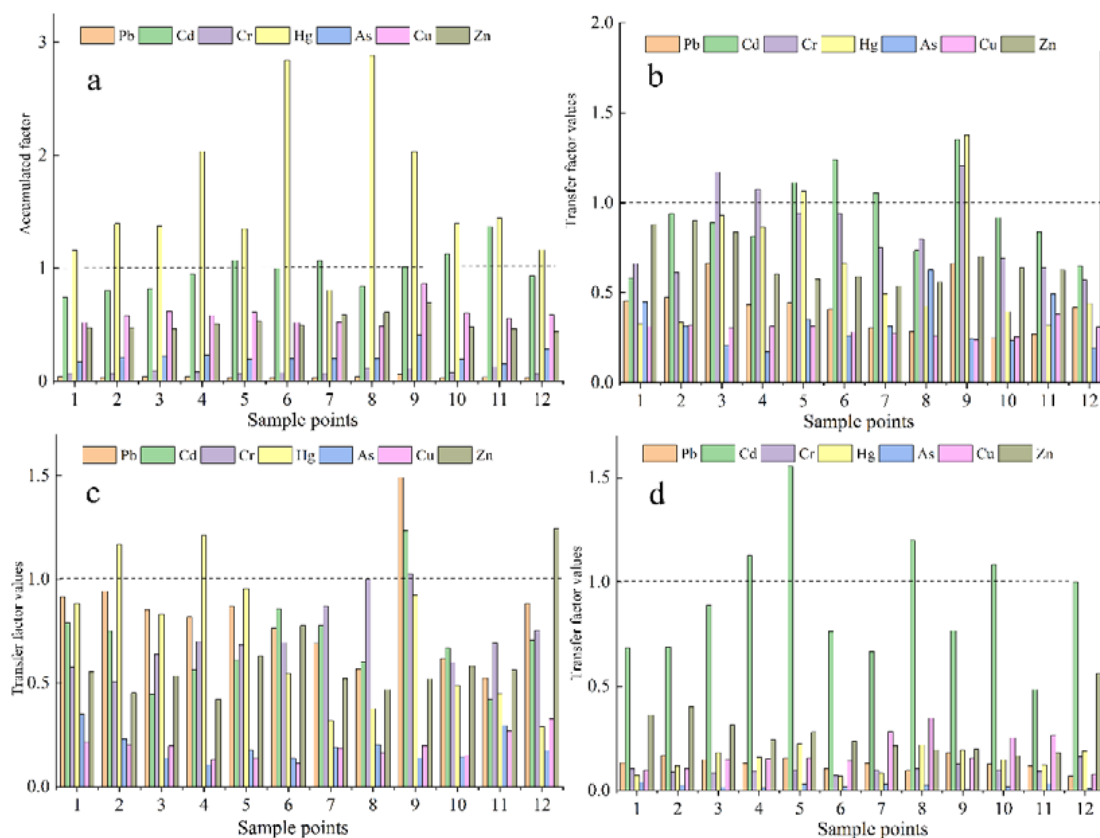


Figure 5. RSP (a) and RCD (b) values of HMs' speciations in paddy soil ( $n = 12$ ).

### 3.3. Accumulated and Transfer Factors in Root, Stem, Leaves and Grain of Rice

The BCF and TF coefficients of different parts of rice were varied, which can be used to reflect the absorption and transport capacity of plants for HMs. Figure 6a shows that the BCF values for Cd, Zn, Cu, Pb, Hg, Cr and As accumulated in rice were 0.74–1.37, 0.44–0.70, 0.49–0.86, 0.03–0.06, 0.81–2.88, 0.07–0.13 and 0.15–0.41, respectively. The order of BCF values for HMs was Hg ( $1.66 \pm 0.63$ ) > Cd ( $0.99 \pm 0.17$ ) > Cu ( $0.59 \pm 0.09$ ) > Zn ( $0.52 \pm 0.07$ ) > As ( $0.22 \pm 0.06$ ) > Cr ( $0.09 \pm 0.02$ ) > Pb ( $0.04 \pm 0.01$ ). The TF values of Cd, Zn, Cu, Pb, Hg, Cr and As from rice root to stem were 0.58–1.35, 0.54–0.1.84, 0.24–0.38, 0.25–0.66, 0.32–1.38, 0.57–0.21 and 0.17–0.63, respectively (Figure 6b). The order of TF values for HMs was Cd ( $0.93 \pm 0.22$ ) > Cr ( $0.84 \pm 0.21$ ) > Zn ( $0.77 \pm 0.34$ ) > Hg ( $0.64 \pm 0.33$ ) > Pb ( $0.42 \pm 0.13$ ) > Cu ( $0.30 \pm 0.04$ ) > As ( $0.32 \pm 0.13$ ). The TF values of Cd, Zn, Cu, Pb, Hg, Cr and As from rice root to leaves were 0.42–1.24, 0.42–0.1.24, 0.11–0.33, 0.52–1.49, 0.29–1.21, 0.50–1.02 and 0.11–0.34, respectively (Figure 6c). The order of the TF values for HMs was Pb ( $0.83 \pm 0.24$ ) > Cr ( $0.73 \pm 0.15$ ) > Hg ( $0.70 \pm 0.31$ ) > Cd ( $0.70 \pm 0.21$ ) > Zn ( $0.61 \pm 0.21$ ) > Cu ( $0.19 \pm 0.06$ )  $\approx$  As ( $0.19 \pm 0.07$ ). The TF values of Cd, Zn, Cu, Pb, Hg, Cr and As from rice root to grains were 0.48–1.56, 0.17–0.56, 0.07–0.35, 0.07–0.18, 0.07–0.22, 0.07–0.16, 0.01–0.04, respectively (Figure 6d). The order of the TF values for these HMs was Cd ( $0.91 \pm 0.28$ ) > Zn ( $0.28 \pm 0.11$ ) > Cu ( $0.18 \pm 0.08$ ) > Hg ( $0.15 \pm 0.05$ ) > Pb ( $0.13 \pm 0.03$ ) > Cr ( $0.10 \pm 0.02$ ) > As ( $0.02 \pm 0.01$ ). Overall, for the AF values, although Hg and Cd were more easily accumulated in rice, Cd was more easily transferred from root to grain from the perspective of TF values in comparison with other HMs and metalloids. This indicated that there was a strong mobility of Cd from the soil to rice, and this may pose a potential risk to local residents. Therefore, better management practices are required to reduce the high accumulation of HMs with high TFs. In addition, more attention should be paid to the accumulation of different HMs and the transfer of HMs to crops other than rice, such as vegetables and fruits.



**Figure 6.** The accumulated factor in rice (a), transfer factor from root to stems (b), transfer factor from root to leaves (c) and transfer factor from root to grains (d) ( $n = 12$ ).

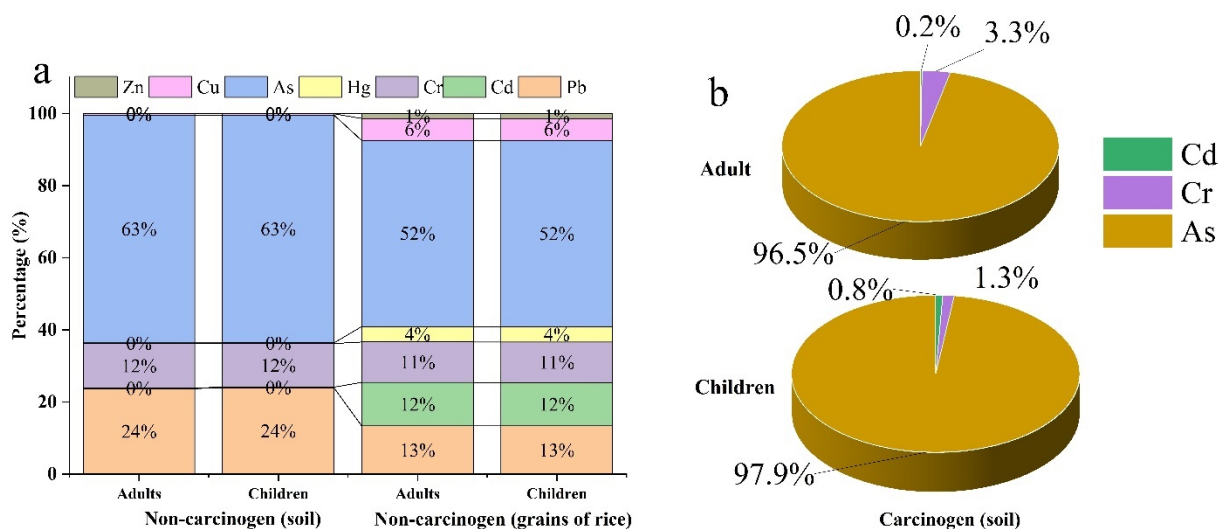
### 3.4. Health Risk Assessment of HMs in Soil and Rice

Table 2 shows that the non-carcinogenic health risk index under different exposure routes for the same HMs was successively  $HQ_{oral}$ ,  $HQ_{dermal}$  and  $HQ_{inh}$ . The average HQ value of each type of HM for adults was less than 1, reflecting that there was no non-carcinogenic risk of individual HMs in the soil to adults and children in the study area. The non-carcinogenic risk order of different HMs for adults was  $As > Cr > Pb > Zn > Hg > Cr > Cu$ , and for children it was  $As > Pb > Cr > Cu > Zn > Hg > Cd$ . For adults, the HI value of HMs in the soil was  $1.18 \times 10^{-2} \pm 2.21 \times 10^{-3}$ , and  $7.62 \times 10^{-2} \pm 1.42 \times 10^{-2}$  for children. This indicated that HMs in the soil posed a higher potential risk to local children, and most of these risks were caused by As and Pb in the soil. The Pb, Cd, Cr, Hg, As, Cu and Zn concentrations in rice grains without husk in this study were  $0.26 \pm 0.07$ ,  $0.17 \pm 0.05$ ,  $0.47 \pm 0.12$ ,  $0.02 \pm 0.00$ ,  $0.22 \pm 0.07$ ,  $3.41 \pm 1.16$  and  $5.87 \pm 1.06$ , respectively. For adults and children, the HI values of rice grains were  $4.15 \pm 0.71$  and  $21.70 \pm 3.76$ , respectively, indicating that HMs can pose a huge health risk to local residents through food intake. Taken together, the non-carcinogenic risk of HM pollution to children in this study area was higher than that of adults, and As was still the main risk factor for both children and adults (Figure 7a). In addition, according to the non-carcinogenic risk contribution rates of multimedia HM exposure, the contribution rates of dietary food (ingestion) were very large. This result illustrated that locally produced foods may be the main exposure routes causing non-carcinogenic HM risk to local residents. In order to maintain the health of the residents in the study area, it is strongly recommended to conduct a health risk assessment on other crops grown in the area, and transporting foods and vegetables from other areas can not only meet the living needs of residents, but also reduce the occurrence of non-carcinogenic health risks. Furthermore, from the contribution rates of the multimedia and multipathway total HQ values to total HI, As was the most significant non-carcinogenic risk factor. Therefore, strengthening the control of As pollution in the study area is an important task to ensure the health of local residents.

**Table 2.** The non-carcinogenic health risk of HMs in paddy soil and rice grains ( $n = 12$ ).

| Exposure Pathways     | Population      | HQ Values                 |                           |                           |                           |                           |                           |                           | HI                        |
|-----------------------|-----------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
|                       |                 | Pb                        | Cd                        | Cr                        | Hg                        | As                        | Cu                        | Zn                        |                           |
| Inhalation (Soil)     | Adults          | $9.92 \times 10^{-6} \pm$ | $1.25 \times 10^{-6} \pm$ | $5.16 \times 10^{-4} \pm$ | $6.99 \times 10^{-8} \pm$ | $2.59 \times 10^{-5} \pm$ | $1.46 \times 10^{-7} \pm$ | $3.88 \times 10^{-8} \pm$ | $1.11 \times 10^{-3} \pm$ |
|                       | (Mean $\pm$ SD) | $2.71 \times 10^{-6a}$    | $1.38 \times 10^{-7a}$    | $1.15 \times 10^{-4a}$    | $2.07 \times 10^{-8a}$    | $4.47 \times 10^{-6a}$    | $1.59 \times 10^{-8a}$    | $3.20 \times 10^{-9a}$    | $2.44 \times 10^{-4a}$    |
|                       | Children        | $4.68 \times 10^{-5} \pm$ | $5.89 \times 10^{-6} \pm$ | $2.44 \times 10^{-3} \pm$ | $3.30 \times 10^{-7} \pm$ | $1.22 \times 10^{-4} \pm$ | $6.87 \times 10^{-7} \pm$ | $1.83 \times 10^{-7} \pm$ | $5.23 \times 10^{-3} \pm$ |
|                       | (Mean $\pm$ SD) | $1.28 \times 10^{-5b}$    | $6.49 \times 10^{-7b}$    | $5.43 \times 10^{-4b}$    | $9.75 \times 10^{-8b}$    | $2.11 \times 10^{-5b}$    | $7.48 \times 10^{-8b}$    | $1.51 \times 10^{-8b}$    | $1.15 \times 10^{-3b}$    |
| Dermal contact (Soil) | Adults          | $5.38 \times 10^{-5} \pm$ | $1.55 \times 10^{-5} \pm$ | $1.07 \times 10^{-3} \pm$ | $4.74 \times 10^{-6} \pm$ | $4.21 \times 10^{-3} \pm$ | $7.91 \times 10^{-7} \pm$ | $1.05 \times 10^{-6} \pm$ | $1.07 \times 10^{-2} \pm$ |
|                       | (Mean $\pm$ SD) | $1.47 \times 10^{-5a}$    | $1.71 \times 10^{-6a}$    | $2.38 \times 10^{-4a}$    | $1.40 \times 10^{-6a}$    | $7.28 \times 10^{-4a}$    | $8.60 \times 10^{-8a}$    | $8.68 \times 10^{-8a}$    | $1.97 \times 10^{-3a}$    |
|                       | Children        | $3.56 \times 10^{-4} \pm$ | $1.03 \times 10^{-4} \pm$ | $7.07 \times 10^{-3} \pm$ | $3.14 \times 10^{-5} \pm$ | $2.79 \times 10^{-2} \pm$ | $5.23 \times 10^{-6} \pm$ | $6.97 \times 10^{-6} \pm$ | $7.10 \times 10^{-2} \pm$ |
|                       | (Mean $\pm$ SD) | $9.75 \times 10^{-5b}$    | $1.13 \times 10^{-5b}$    | $1.58 \times 10^{-3b}$    | $9.29 \times 10^{-6b}$    | $4.82 \times 10^{-3b}$    | $5.69 \times 10^{-7b}$    | $5.75 \times 10^{-7b}$    | $1.30 \times 10^{-2b}$    |
| Sum                   | Adults          | $6.37 \times 10^{-5} \pm$ | $1.68 \times 10^{-5} \pm$ | $1.59 \times 10^{-3} \pm$ | $4.81 \times 10^{-6} \pm$ | $4.24 \times 10^{-3} \pm$ | $9.37 \times 10^{-7} \pm$ | $1.09 \times 10^{-6} \pm$ | $1.18 \times 10^{-2} \pm$ |
|                       | (Mean $\pm$ SD) | $1.74 \times 10^{-5a}$    | $1.85 \times 10^{-6a}$    | $3.53 \times 10^{-4a}$    | $1.42 \times 10^{-6a}$    | $7.32 \times 10^{-4a}$    | $1.02 \times 10^{-7a}$    | $9.00 \times 10^{-8a}$    | $2.21 \times 10^{-3a}$    |
|                       | Children        | $4.03 \times 10^{-4} \pm$ | $1.09 \times 10^{-4} \pm$ | $9.51 \times 10^{-3} \pm$ | $3.17 \times 10^{-5} \pm$ | $2.80 \times 10^{-2} \pm$ | $5.92 \times 10^{-6} \pm$ | $7.15 \times 10^{-6} \pm$ | $7.62 \times 10^{-2} \pm$ |
|                       | (Mean $\pm$ SD) | $1.10 \times 10^{-4b}$    | $1.19 \times 10^{-5b}$    | $2.12 \times 10^{-3b}$    | $9.39 \times 10^{-6b}$    | $4.84 \times 10^{-3b}$    | $6.44 \times 10^{-7b}$    | $5.90 \times 10^{-7b}$    | $1.42 \times 10^{-2b}$    |
| Ingestion (Rice)      | Adults          | $5.53 \times 10^{-1} \pm$ | $5.02 \times 10^{-1} \pm$ | $4.64 \times 10^{-1} \pm$ | $1.79 \times 10^{-1} \pm$ | $2.14 \times 10^{+0} \pm$ | $2.53 \times 10^{-1} \pm$ | $5.81 \times 10^{-2} \pm$ | $4.15 \times 10^{+0} \pm$ |
|                       | (Mean $\pm$ SD) | $1.55 \times 10^{-1a}$    | $1.49 \times 10^{-1a}$    | $1.19 \times 10^{-1a}$    | $6.72 \times 10^{-2a}$    | $6.52 \times 10^{-1a}$    | $8.61 \times 10^{-2a}$    | $1.05 \times 10^{-2a}$    | $7.08 \times 10^{-1a}$    |
|                       | Children        | $1.86 \times 10^{+0} \pm$ | $1.69 \times 10^{+0} \pm$ | $1.56 \times 10^{+0} \pm$ | $6.03 \times 10^{-1} \pm$ | $7.22 \times 10^{+0} \pm$ | $8.53 \times 10^{+0} \pm$ | $1.96 \times 10^{-1} \pm$ | $2.17 \times 10^{+1} \pm$ |
|                       | (Mean $\pm$ SD) | $5.24 \times 10^{-1b}$    | $5.02 \times 10^{-1b}$    | $4.01 \times 10^{-1b}$    | $2.26 \times 10^{-1b}$    | $2.20 \times 10^{+0b}$    | $2.90 \times 10^{+0b}$    | $3.55 \times 10^{-2b}$    | $3.76 \times 10^{+0b}$    |

Note: mean  $\pm$  SD,  $n = 12$ . Different superscript letters in each row represent significant differences between different treatments (ANOVA,  $p < 0.05$ ).



**Figure 7.** The proportion of single HMs for the non-carcinogen risk in soil and rice grains (a), and single HMs for the carcinogen risk in soil (b).

According to the concentrations of HMs in the paddy soil, the individual carcinogenic risk and total carcinogenic risk caused by different exposure pathways to adults and children were calculated (Table 3). Table 3 showed that the CF values of Cd and Cr for adults and children were both within the acceptable range of  $10^{-8}$  to  $10^{-4}$ , but As exceeded the acceptable range. The order of carcinogenic risk for different HMs for adults and children was  $As > Cr > Cd$ . The TCR value was  $1.55 \times 10^{-3} \pm 2.70 \times 10^{-4}$  for adults, and  $2.30 \times 10^{-3} \pm 3.98 \times 10^{-4}$  for children. As, Cr and Cd in the soil had a carcinogenic health risk for adults and children, and the carcinogenic risk was higher for children than for adults. In addition, As was the main carcinogenic factor in comparison to Cr and Cd (Figure 7b). Furthermore, the relevant data showed that the main exposure pathway of soil HMs was hand–mouth ingestion. This finding suggests that people living around the study area should avoid the health hazards posed by the ingestion of the soil through the hand–mouth exposure pathway during production and life activities, which were particularly important for children. The risks of carcinogenesis through dietary crops (rice) were very serious. For adults and children, the CF values of As were greater than  $1 \times 10^{-4}$  in the hand–mouth exposure pathways. The TCRs of the adults and children in the study area caused by exposure to HMs through multiple pathways were  $1.55 \times 10^{-3}$  and  $2.30 \times 10^{-3}$  respectively, which were higher than the US EPA limit value and indicated serious carcinogenic risk. Moreover, from the contribution rates of all CF values to the multipathway TCR, the contribution rate of As was the largest, accounting for 96.5% and 97.9% of adults and children, respectively, followed by Cr, accounting for 3.3% and 1.3% of adults and children, respectively, and the contribution rates of Cd were relatively low. In conclusion, dietary exposure was the most important medium and pathway of exposure to carcinogenic risk. Therefore, it was necessary to strictly control the intake of rice in this area.



**Table 3.** The carcinogenic health risk of Cd, Cr and As in paddy soil.

| Exposure Methods | Population           | CF Values  |  |  | TCF Values   |
|------------------|----------------------|--|--|--|--|
|                  |                      | Cd   | Cr   | As   |  |
| Hand–mouth       | Adults (Mean ± SD)   | $2.96 \times 10^{-6} \pm 3.26 \times 10^{-7}$ <sup>a</sup>   | $5.03 \times 10^{-5} \pm 1.12 \times 10^{-5}$ <sup>a</sup> | $1.49 \times 10^{-3} \pm 2.58 \times 10^{-4}$ <sup>a</sup> | $1.55 \times 10^{-3} \pm 2.70 \times 10^{-4}$ <sup>a</sup> |
|                  | Children (Mean ± SD) | $1.81 \times 10^{-5} \pm 1.99 \times 10^{-6}$ <sup>b</sup>   | $2.52 \times 10^{-5} \pm 5.62 \times 10^{-6}$ <sup>b</sup> | $2.24 \times 10^{-3} \pm 3.87 \times 10^{-4}$ <sup>b</sup> | $2.28 \times 10^{-3} \pm 3.95 \times 10^{-4}$ <sup>b</sup> |
| Inhalation       | Adults (Mean ± SD)   | $4.50 \times 10^{-10} \pm 4.95 \times 10^{-11}$ <sup>a</sup> | $6.20 \times 10^{-7} \pm 1.38 \times 10^{-7}$ <sup>a</sup> | $1.17 \times 10^{-7} \pm 2.02 \times 10^{-8}$ <sup>a</sup> | $7.38 \times 10^{-7} \pm 1.59 \times 10^{-7}$ <sup>a</sup> |
|                  | Children (Mean ± SD) | $2.12 \times 10^{-9} \pm 2.34 \times 10^{-10}$ <sup>b</sup>  | $2.93 \times 10^{-6} \pm 6.52 \times 10^{-7}$ <sup>b</sup> | $5.53 \times 10^{-7} \pm 9.55 \times 10^{-8}$ <sup>b</sup> | $3.48 \times 10^{-6} \pm 7.48 \times 10^{-7}$ <sup>b</sup> |
| Dermal contact   | Adults (Mean ± SD)   | $9.45 \times 10^{-9} \pm 1.04 \times 10^{-9}$ <sup>a</sup>   | $1.60 \times 10^{-7} \pm 3.57 \times 10^{-8}$ <sup>a</sup> | $1.96 \times 10^{-6} \pm 3.38 \times 10^{-7}$ <sup>a</sup> | $2.13 \times 10^{-6} \pm 3.75 \times 10^{-7}$ <sup>a</sup> |
|                  | Children (Mean ± SD) | $6.26 \times 10^{-8} \pm 6.89 \times 10^{-9}$ <sup>b</sup>   | $1.06 \times 10^{-6} \pm 2.36 \times 10^{-7}$ <sup>b</sup> | $1.30 \times 10^{-5} \pm 2.24 \times 10^{-6}$ <sup>b</sup> | $1.41 \times 10^{-5} \pm 2.48 \times 10^{-6}$ <sup>b</sup> |
| Sum              | Adults (Mean ± SD)   | $2.97 \times 10^{-6} \pm 3.27 \times 10^{-7}$ <sup>a</sup>   | $5.11 \times 10^{-5} \pm 1.14 \times 10^{-5}$ <sup>a</sup> | $1.50 \times 10^{-3} \pm 2.58 \times 10^{-4}$ <sup>a</sup> | $1.55 \times 10^{-3} \pm 2.70 \times 10^{-4}$ <sup>a</sup> |
|                  | Children (Mean ± SD) | $1.81 \times 10^{-5} \pm 2.00 \times 10^{-6}$ <sup>b</sup>   | $2.92 \times 10^{-5} \pm 6.50 \times 10^{-6}$ <sup>b</sup> | $2.25 \times 10^{-3} \pm 3.89 \times 10^{-4}$ <sup>b</sup> | $2.30 \times 10^{-3} \pm 3.98 \times 10^{-4}$ <sup>b</sup> |

Note: mean ± SD,  $n = 12$ . Different superscript letters in each row represent significant differences between different treatments (ANOVA,  $p < 0.05$ ).

#### 4. Discussion

The coal mine in Xingren County is one of the typical high-arsenic coal mine areas in southwest Guizhou, and As content in the water body of the research area ranged from 1.19 to 288.50  $\mu\text{g/L}$  [42]. Most mining areas in Xingren county have stopped mining, and many polluted areas have started ecological remediation, which has alleviated the HM pollution in the soil of the study area to some extent. However, from the current research results, the long-term coal mining activities and the local geochemical background make the HM pollution in the study area still serious [43]. In the study area, the soil physical and chemical indicators (including soil pH, SOM and N) were relatively low. The contents of As seriously exceeded the standard value, and became the main pollution factor. Although the contents of Cd in soil did not exceed the limit value, the percentage of the Cd exchangeable fraction was significantly higher than that of other HMs, which indicated that Cd may be more easily absorbed by rice. The combined results of the RSP and RAC ecological risk assessments indicated that Cd in the soil of the study area was of high ecological risk, which may be related to the weak acidity of the soil in the study area. It was known that the effectiveness of Cd was largely affected by the soil pH. The lower the soil pH, the higher the effectiveness of Cd and the easier it was for plants to take up [44]. It was worth noting that although the contents of As in the soil of the study area were much higher than the limit value, the exchangeable fraction accounted for a relatively small proportion, and the residual fraction accounted for a relatively high proportion. Rice is generally planted in a flooded anaerobic environment, and the availability of As in soil is high. Meanwhile, its root silicon channel has the ability to efficiently absorb As (III), which leads to a significantly higher concentration of As in rice than in other grain crops [45]. In the current research, the AF and TF values of As in rice were relatively low, but the underlying mechanism was still unclear. Furthermore, the non-carcinogenic and carcinogenic risks of HMs in the soil and rice grains in the study area were greater than the acceptable ranges. As was the most significant non-carcinogenic heavy metal and carcinogenic heavy metal. As, Pb and Cr had varying degrees of non-carcinogenic risk, while As, Cr, and Cd had varying degrees of carcinogenic risk. Compared to adults, heavy metals in the soil posed a higher health risk to local children, and hand–mouth and ingestion were the main exposure routes. Crops absorb heavy metals from the soil, and the heavy metals are concentrated in the edible parts of the crops, which can harm human health through the food chain. The grains and vegetables used by the population in the study area were mainly produced in the area, and the HMs in grains and vegetables were mainly from the soil. Therefore, it is of great significance to carry out the source apportionment of As, Pb, Cd and Cr in the soil and crops (all crops grown in the study area including rice) in the study area. Although this study has evaluated the characteristics, chemical speciations and health risks of HMs in paddy soil and rice in the study area, there were still multiple uncertainties. Firstly, the representativeness and homogeneity of the samples, population sampling, accuracy of exposure parameters and model stability seriously affect the health risk assessment results of the HM exposure, so the uncertainty of the risk assessment is widespread [31,46,47]. The relatively small sample size and the single crop in this study may lead to some variation in the results. Secondly, there are differences in the dietary habits, lifestyle and physical characteristics of the different age groups, and the parameters used for the health risk assessment in this study were obtained from the Guizhou statistical yearbook and the US EPA and Chinese population exposure parameter manual, so the information thus obtained may not be fully appropriate for the region and may lead to the deviation in the evaluation results. Nevertheless, this study provided a preliminary understanding of the current status of HM pollution and the health risks of population exposure around the coal mining area in Xingren county, and it provided an important basis for prioritizing the management of health risks and environmental risks in the study area.

## 5. Conclusions

This study showed that the physical and chemical indexes of soil in the study area were relatively low, and the soil and rice in the study area were contaminated with HMs to varying degrees. The As contents in the soil seriously exceeded the standard value, but surprisingly, we did not find high AF and TF values of As in the rice. The lower activity of As in soil rendered it difficult to be absorbed by rice, which may be the main reason for the lower AF and TF values of As in rice. The Cd content in the soil did not seriously exceed the standard, but the percentage of the exchangeable fraction, AF and TF values in the rice were significantly higher than those other HMs, suggesting that it may be more readily absorbed by rice and then enter the food chain as a threat to human health. The health risks of different HMs to children caused by different exposure pathways were higher than those for adults, and As was the major risk factor for both children and adults according to the results of the HM health risk assessment. The total non-carcinogenic and carcinogenic risk indexes in adults and children were relatively high, which were caused by HM exposure through ingesting rice husk, thus indicating serious non-carcinogenic and carcinogenic risks. Among the evaluated pathways, the contribution rate of hand–mouth and ingestion were the largest. It thus appeared that HMs in the soil and rice in the study area have posed a high potential health risk to the local residents, and effective measures should be taken in time to mitigate the local contamination of HMs and the health risks posed by them. Biochar, as an ecologically and environmentally friendly material, can be used to improve the soil environment in the study area.

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