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Pollution, Risk and Transfer of Heavy Metals in Soil and Rice: A Case Study in a Typical Industrialized Region in South China

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Abstract: Rice paddies in industrialized areas are particularly impacted by heavy metal contaminations. Based on 205 pairs of soil and rice samples collected from Yingtan, a typical industrialized region in southern China, the work was carried out to investigate the characteristics of heavy metals in soils and rice, evaluate their corresponding health risks to local residents and elucidate the migration and enrichment patterns of the trace elements from soil to rice. Approximately 98.5%, 77.6% and 70.2% of the soil samples were polluted by Cd, Pb and Cu, while 34.6%, 23.4% and 15.6% of the rice grain samples had contents of Cd, As and Pb exceeding the standard limitations, respectively. Consuming locally produced rice posed serious risks to local residents. The non-carcinogenic risks were primarily due to dietary intake of *i*-As and Cd, and carcinogenic risks were mainly caused by *i*-As in rice grains. Cd is most likely to be migrated and enriched. The bioaccumulation process is influenced by a combination of environmental factors, such as soil pH, TOC, heavy metal contents in bioavailable fractions and mineral elements, such as Al, Mn and Fe. The findings help in making effective pollution prevention and control regulations for guaranteeing the health of local residents.

Keywords: heavy metals; soil contamination; rice grain; health risk assessment; migration; enrichment

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1. Introduction

Intensive industrial activities, especially the mining and smelting processes, can lead to numerous emissions of heavy metals into the environment [1,2]. Due to their persistence and potential toxicity, the accumulation of heavy metals in soils, as well as their subsequent bioaccumulation in crops and vegetables, have gained wide attention from the public and researchers [3–5]. Chronic exposure to Cd in soils and foods may lead to prostatic proliferative lesions, bone fracture, kidney dysfunction and hypertension [6]. Intake of inorganic As may cause skin cancer, bladder and lung cancer as well as nervous system disorders [7–9]. Pb may have adverse effects on the growth and development of children, such as reduced intelligence and short-term memory loss [10]. Although their toxicity is relatively low, long-term exposure to excessive Cu, Zn, Cr and Ni may cause kidney and liver problems, brain damage and developmental retardation [11,12].

Many studies have been conducted to assess the heavy metal contamination in soils and crops and the corresponding risks to human beings [1,2,13–16]. The inhalation, dermal contact and ingestion of contaminated soils would directly lead to health risks in adults and children [17,18]. Excessive heavy metals in soil can result in their accumulation and enrichment in crops and vegetables. Rice, the most important cereal food in south China, is more likely to enrich trace elements, such as Cd and As, in the edible parts [19,20]. The dietary consumption of rice is an important pathway for human exposure to the toxic elements [21,22]. China has a high daily intake of rice per capita (214.9 g/day), which is almost half higher than the average value worldwide (148 g/day) [23]. It is important to evaluate the risks caused by heavy metals in soil and rice and identify the major pollutants and pathways for policymaking.

To develop efficient pollution control and soil remediation measures, it is critical to understand the transfer behaviors of heavy metals in the soil–rice system. The uptake of heavy metals from soils to plants can be governed by multiple factors, including the physiological characteristics of rice plant, the properties of the soil, the total contents and chemical speciation of the heavy metals in soils and other environmental conditions [3,24,25]. It has been well recognized that metal mobility and availability in soils are critical for their bioaccumulations. In general, only dissolved and exchangeable parts of heavy metals in soils can be absorbed and transported by plants, whereas the insoluble precipitation and structural components of lattices in soils cannot be utilized [26,27]. The soil pH and organic matter contents were found to play important roles in controlling the adsorption and desorption behavior of heavy metals onto soils [28,29]. Based on pot experiments and field investigations, multiple methods have been implemented to explore the relationships between heavy metals in rice and soils, including correlation analysis, linear regression, discriminant analysis, random forest and gradient boosting [12,30–32].

Yingtan, located in the northeast of Jiangxi Province in south China, covers an area of 3.55×10^3 km^2 and hosts a population of more than 1.1 million (Figure 1). The region is rich in mineral resources, including silver, lead and zinc, and gypsum ores, which are mainly concentrated in the southern area. During the last two decades, the industrial GDP of Yingtan has grown threefold. Non-ferrous metal mining, smelting and the processing industry accounted for approximately 70.9% of the total values in 2020 [33]. Currently, the city is known as the "copper capital of China". As shown in Figure 1, most mineral mining and processing activities occurred in Guixi, and Guixi copper smelting plant has been the largest copper industry base in China and Asia [33]. While intensive mining and smelting activities have greatly promoted local economic development, numerous heavy metals were emitted into the environment from the anthropogenic sources. According to the Ecology and Environment Bureau of Yingtan, approximately two thirds of the key supervision enterprises for soil pollution in the area were copper, lead and zinc smelting plants [34]. Except the mining and processing activities, industries, including biopharmaceuticals, mechanical metallurgy, dyeing and chemical production, would also contribute to the heavy metal pollution in the study area. With a warm climate and abundant rainfall, Yingtan is also an important agricultural base in Jiangxi Province, and paddy rice is the dominant crop in the area. In order to establish effective pollution prevention and control regulations for guaranteeing the health of local residents, it is urgent to assess the pollution levels and corresponding risks, understand the bioaccumulation of heavy metal in the soil–rice system and identify the controlling variables in the process. This work was conducted to investigate the characteristics of heavy metal contents in paddy soils, rice grains and husks based on a field survey. The health risks posed by the heavy metals in soils and rice grains were estimated for local residents, and the key elements and pathways were identified. The final objective was to find the potential controlling factors for the transfer of toxic metals from soils to rice grains and construct models for predicting the bioaccumulation behaviors of the trace elements in the soil–rice system.

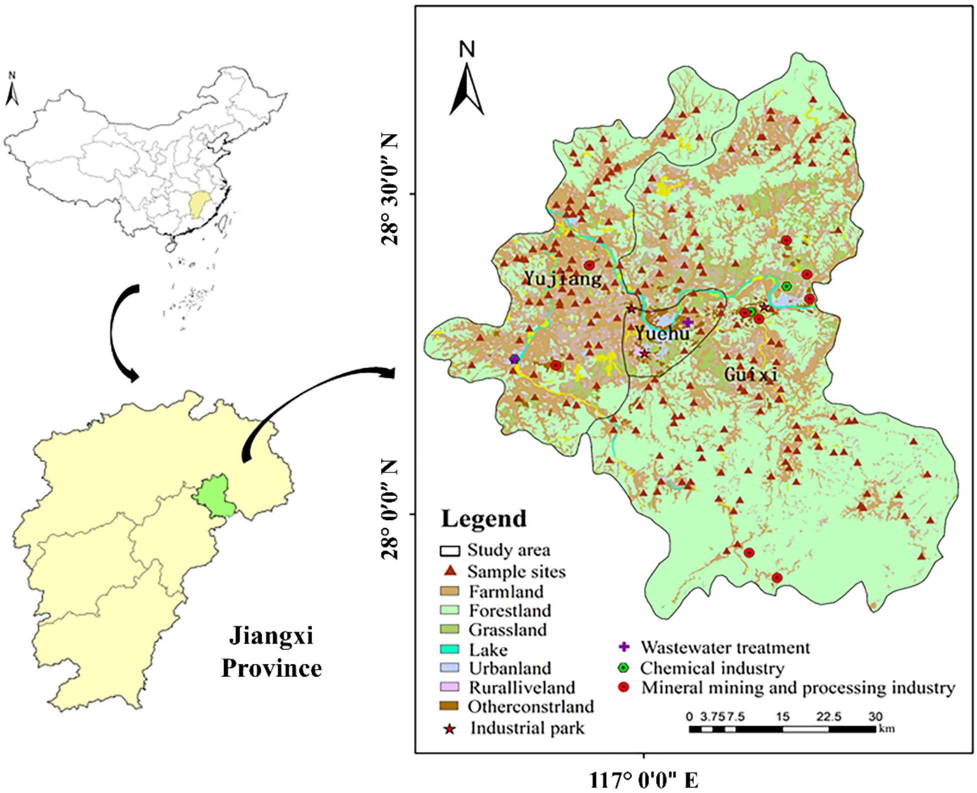

Figure 1. Distribution of potential sources of heavy metals and soil sampling points in the study area.

2. Materials and Methods

2.1. Sample Collection, Preparation and Analysis

As shown in Figure 1, 205 sets of soil and rice samples were collected in Yingtan farmlands in September 2017, with sampling sites evenly distributed in the paddy fields of the study area. To avoid the direct impacts of traffic exhaustion, the sampling points were at least 500 m away from the main roads. At each site, ten or more healthy and mature rice plants were collected randomly, and the corresponding surface soil samples (0~20 cm) were collected from the roots of these rice plants. All samples were sealed in plastic bags and transported back for lab preparation and analysis. The soil samples were air-dried naturally at room temperature. After removing stones, gravel, and plant debris, the soils were grounded and passed through a 2 mm nylon sieve. The rice samples were dried to obtain constant weights. The rice husks were separated from rice grains by a small shelling machine, and both of them were milled into powders using an agate ball mill. The sieved soil samples and milled rice grain and husk samples were collected and stored in PTFE bottles at 4 °C for further chemical analysis.

According to method 3052 of the U.S. Environmental Protection Agency (USEPA), the soil powder samples were digested by a microwave digestion system (MARS, CEM, Matthews, NC, USA), and the concentrations of heavy metals in the achieved solutions were measured using an inductively coupled plasma-mass spectrometer (ICP-MS, NexION 350D, PerkinElmer, Waltham, MA, USA) (Figure S1). The contents of heavy metals in different chemical fractions were analyzed following the modified BCR continuous extraction method [35,36]. Rice grain and husk samples were digested using nitric acid and hydrogen peroxide mixture [37]. The chemical species of As in rice grains were determined using a microwave-assisted extraction method followed by detection with an Altus A10 HPLC (PerkinElmer, Waltham, MA, USA) hyphenated to ICP-MS, which had been reported in our previous study [38]. For the purpose of quality assurance and quality control (QA/QC), certified reference materials were used, including SRM 1646A from National Institute of Standards and Technology of the U.S., and GSS6, GSS7 and GSS16 from the Chinese Academy of Geological Sciences. Duplicated samples (20% of the total) and blank controls were routinely analyzed in each batch of sample digestion and chemical analysis. Soil pH was measured by a pH meter by making a suspension (soil-to-water ratio 1:5), followed by centrifuging after sufficient shaking. Total organic carbon (TOC) in soil was measured by a TOC analyzer (TOC-LCPH, Shimadzu, Tokyo, Japan) coupled with an SSM-5000A unit.

2.2. Health Risk Assessment

In this study, the human health risks, including carcinogenic and non-carcinogenic risks, were assessed using models established by the US Environmental Protection Agency. Firstly, the average daily intake (*ADI*, mg/kg/day) values for each investigated metal and exposure pathway are calculated as follows:

$$ADI_{\text{rice}} = \frac{C_{rice} \times IR \times EF \times ED}{AT \times BW} \tag{1}$$

$$ADI_{\text{ing}} = \frac{C_{soil} \times I_{ng}R \times EF \times ED}{AT \times BW} \times 10^{-6} \tag{2}$$

$$ADI_{\text{der}} = \frac{C_{soil} \times SA \times AF \times ABS \times EF \times ED}{AT \times BW} \times 10^{-6} \tag{3}$$

$$ADI_{\text{inh}} = \frac{C_{soil} \times I_{nh}R \times EF \times ED}{PEF \times AT \times BW} \tag{4}$$

where ADI_{rice} represents the average daily intake (mg/kg/day) of the investigated heavy metal through rice ingestion, while ADI_{ing}, ADI_{der} and ADI_{inh} are average daily intake (mg/kg/day) through ingestion, dermal contact and inhalation of soils. C_{rice} and C_{soil} are the heavy metal contents (mg/kg) in rice and soil, respectively. IR, $I_{ng}R$ and $I_{nh}R$ are the rice ingestion rate (kg/day), soil ingestion rate (mg/day) and inhalation rate (m^3/day), respectively. EF is the exposure frequency (day/year), ED is the duration of exposure (year), AT is time period over which the daily intake is averaged (day), BW is the average body weight (kg) of the investigated individuals, SA is the dermal contact area (cm^2), AF is soil-to-skin adherence factor (mg/cm^2/day), ABS is the absorption factor (unitless) and PEF is the soil to air particulate emission factor (m^3/kg). In general, AT is equal to the duration of exposure (ED) for non-carcinogenic effects. Based on Equations (1)–(4), the lifetime average daily intake (LADI, mg/kg/day) is calculated similarly, with the parameter AT set to a lifetime of 76.6 years [39]. The parameters used in the health risk models are shown in Table S1.

Based on the estimated levels of human exposure, the non-carcinogenic and carcinogenic health risks are estimated as:

$$HI_j = \sum HQ_{ij} = \sum \frac{ADI_{ij}}{RfD_{ij}} \tag{5}$$

$$ILCR_j = \sum ILCR_{ij} = \sum LADI_{ij} \times SF_{ij} \tag{6}$$

where i and j represent the heavy metal i and exposure path j, respectively. HQ and HI are the hazard quotient and hazard index, respectively, representing the potential non-carcinogenic health risk resulting from exposure to individual and multiple trace metals. $ILCR$ is the incremental lifetime cancer risk, indicating the incremental probability of cancer development due to the exposure to a given carcinogenic chemical. RfD_{ij} and SF_{ij} are the reference dose (mg/kg/day) and carcinogenic slope factor ((mg/kg/day)$^{-1}$) of heavy metal i under the jth exposure pathway. The reference RfD and SF values used in the study are shown in Table S2.

2.3. Migrations of Heavy Metals from Soil to Rice

Many heavy metals in soil can accumulate in edible parts of crops. To evaluate the accumulation capabilities of various trace elements, the bioconcentration factor (BCF) is defined as the ratio of the concentrations of heavy metals in the crop plant to the concentrations of heavy metals in the soils. In the study, the BCFs for rice grain and husk were calculated as follows:

$$BCF_{rice/soil} = \frac{C_{rice}}{C_{soil}} \tag{7}$$

$$BCF_{husk/soil} = \frac{C_{husk}}{C_{soil}} \tag{8}$$

where C_{rice} and C_{husk} are the content of heavy metal in rice grain and husk (mg/kg), respectively, and C_{soil} is the concentration of heavy metal in the corresponding soil sample (mg/kg).

The transfer of heavy metals from soil to rice grain is an extremely complicated procedure comprehensively affected by various factors. In the study, the investigated impact factors included soil properties (soil pH and TOC), chemical speciation of heavy metals in soils and the contents of mineral elements Fe, Mn and Al in soils. Pearson's correlation analysis was applied to identify potential controlling factors for the migration of heavy metals from soil to rice grain, and stepwise regressions were used to build multiple linear regression models explaining the BCFs as functions of the identified factors [40]. The general form of the models can be written as follows:

$$\log(BCF) = a_0 + \sum a_i \times \log(x_i) \tag{9}$$

where a_i is the estimated coefficient for impact factor x_i. Both BCF and the explanatory variables were log-transformed.

3. Results and Discussion

3.1. Heavy Metals in Soils and Rice

Table 1 summarizes the descriptive statistics of total contents of heavy metals in agricultural soil samples collected from the study area as well as their soil background values in Jiangxi Province and risk screening values in paddy fields. The average contents of heavy metals in the surface soil were 53.1, 20.5, 27.9, 8.15, 0.335, 44.5 and 182 mg/kg for Cr, Ni, Cu, As, Cd, Pb and Mn, respectively. It was noticed that trace elements Cr, Ni, Cu, Cd and Pb had their mean contents higher than their corresponding background values in the surface soils of Jiangxi Province. The percentages of soil samples having their metal concentrations exceeding the corresponding background values followed the decreasing order of Cd (98.5%) > Pb (77.6%) > Cu (70.2%) > Ni (47.8%) > Cr (41.5) > As (23.9%) > Mn (9.30%), indicating that the contents of Cd, Pb and Cu in soils had been significantly elevated by anthropogenic emissions in the study area. In addition, 57.1%, 4.39%, 0.98% and 0.49% of the soil samples had their Cd, Cu, Pb and As concentrations exceeding their corresponding risk screening values set for paddy fields, suggesting the urgent needs of quality monitoring and pollution control measures. According to the results, Cd is one of the most important soil pollutants in the study area due to its high contents and toxicity.

Table 1. Descriptive statistical analysis of total heavy metals in soils (mg/kg).

Heavy Metal	Mean	STD	Max	Min	Background Value [a]	Risk Screening Value [b]				P_{SBV} (%) [c]	P_{RCV} (%) [d]
						pH ≤ 5.5	5.5 < pH ≤ 6.5	6.5 < pH ≤ 7.5	pH >7.5		
Cr	53.1	41.5	181	8.22	48.0	250	250	300	350	41.5	0.00
Ni	20.5	9.59	45.2	3.59	19.0	60	70	100	190	47.8	0.00
Cu	27.9	11.1	63.6	8.00	20.8	50	50	100	100	70.2	4.39
As	8.15	4.75	36.9	1.38	10.4	30	30	25	20	23.9	0.49
Cd	0.335	0.121	0.816	0.066	0.100	0.3	0.4	0.6	0.8	98.5	57.1
Pb	44.5	16.4	87.2	9.20	32.0	80	100	140	240	77.6	0.98
Mn	182	136	1120	26.3	328	-	-		-	9.30	-

Note: [a]: the soil background value for Jiangxi Province [41]. [b]: the risk screening values for soil contamination in agricultural land (GB 15618–2018) [42]. [c]: percentage of samples having metal concentration exceeding the corresponding soil background value. [d]: percentage of samples having metal concentration exceeding the corresponding risk screening value.

Figure 2 presents distribution patterns of the heavy metals in acid-extractable, reducible, oxidizable and residual fractions based on the modified BCR sequential extraction method. The results suggested significant differences among chemical fractions of the investigated elements. Cd mainly occurred in the acid-extractable fraction (64.2%) in the farmland soils, while the majority of Cr (77.6%), Ni (78.5%), Cu (50.3%), As (66.6%) and Pb (44.7%) were found in the residual fractions. The percentage of mobile fractions of Cd was much larger than the others, indicating that it can easily transfer from soil to plant and may pose severe threats to human health. The residual and oxidizable fractions of Cr and Ni were relatively high (more than 90%), indicating their low migration ability. Cu had more than a 25% content in the oxidizable fraction for its capacity of combining with organic matters in soils and forming complexes and compounds, such as copper sulfide [43]. Except the residual fraction, a large amount of Pb was found in the reducible fraction (39.1%), which was consistent with the previous studies [44,45], for iron and manganese hydroxides can effectively adsorb Pb^{2+} in soils [46,47]. The proportions of the acid-extractable fractions of As were low (2.7%), while those of the oxidizable and reducible fractions were considerable (17.3% and 13.4%).

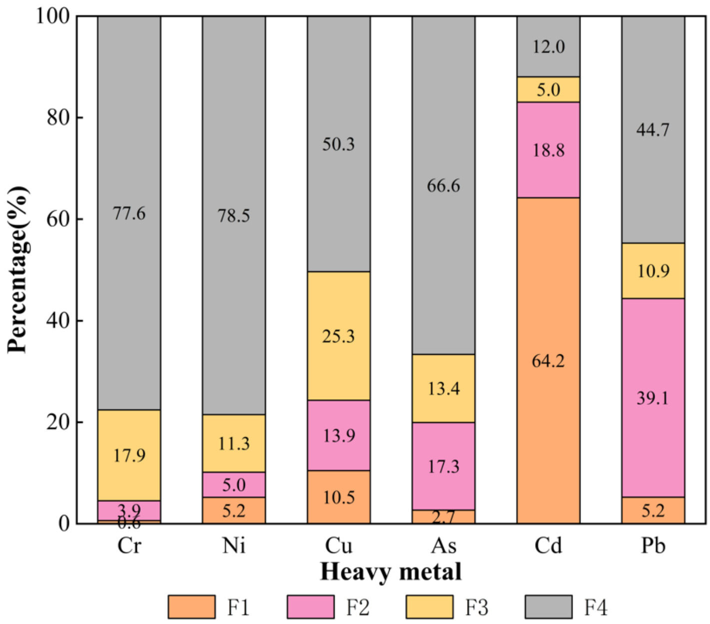

Figure 2. The chemical speciation of heavy metals in soils based on the modified BCR continuous extraction method. F1, F2, F3 and F4 represent the acid-extractable, reducible, oxidable and residual fraction, respectively.

Table 2 shows the basic information for the total amount of investigated heavy metals in rice grain and husk samples. Overall, the average contents of Cr, Ni, Cu, As, Cd and Pb in rice were 0.244, 0.809, 3.49, 0.188, 0.195 and 0.131 mg/kg, respectively. The contents of heavy metals in rice husk were significantly higher than those in rice grains, indicating that rice husk had higher enrichment capacity for heavy metals than rice grains. Previous studies have confirmed that Cr, Ni, Cu, As, Cd and Pb in paddy rice plants were most enriched in the roots, followed by the stems and leaves, rice husk and finally in the rice grain parts [48,49]. The mean ratios of heavy metals in rice grain to those in rice husk followed the order of Cu (0.831) > Cd (0.752) > Ni (0.363) > As (0.169) > Cr (0.144) > Pb (0.061), confirming the significant difference among the enrichment patterns of heavy metals in rice plant. Compared with the corresponding food standards, all the investigated heavy metals except Ni had their contents exceeding the limitations in some rice grain samples, with the frequency in the following decreasing order: Cd (34.6%) > As (23.4%) > Pb (15.6%) > Cr (1.95%) > Cu (1.32%). The exceedance rates of Cd, As and Pb were much higher than Cr and Cu. The high exceedance can be partially attributed to the fact that the concentrations of elements, such as

Cd, in the soils have been significantly elevated by industrial activities, such as mining and smelting, in the study area (Table 1). However, it was found that the order of heavy metal exceedance rates in rice grain is not consistent with that in soils, indicating the impacts from other factors, such as the characteristics of heavy metals and soil properties. In particular, although As had lower contents than both background and risk screen values in most soil samples, it had high exceeding frequency observed in rice grain.

Table 2. Descriptive statistical analysis of total heavy metals in rice grain and husk(mg/kg).

Heavy Metals	Mean		Std		Max		Min		Ratio [a]	Limitation Value		P_{exc} (%) [d]
	Grain	Husk	Grain	Husk	Grain	Husk	Grain	Husk		National Food Safety [b]	Agricultural Industry [c]	
Cr	0.244	1.70	0.224	0.941	1.84	4.51	0.028	0.260	0.144	1.0	1.0	1.95
Ni	0.809	2.23	0.521	1.23	2.93	6.37	0.094	0.409	0.363	-	-	-
Cu	3.49	4.20	1.81	1.89	12.3	9.97	0.369	0.824	0.831	-	10.0	1.32
As	0.188	1.11	0.099	0.729	0.533	3.10	0.032	0.107	0.169	0.26 (*i*-As)	0.7 (total)	23.4
Cd	0.195	0.259	0.151	0.129	1.12	0.780	0.025	0.080	0.752	0.2	0.2	34.6
Pb	0.131	2.15	0.101	0.533	1.02	2.97	0.017	0.598	0.061	0.2	0.4	15.6

Note: [a]: the mean of ratios of heavy metals in rice grain to those in rice husk. [b]: the limitations of metals in rice obtained from the national food safety standards GB 2762-2017 [50]. [c]: the limitations of metals in rice obtained from agricultural industry standards NY861-2004 [51]. [d]: the percentage of rice grain samples having the concentration exceeding the limitation values. In the case that the two standard values were different, the lower was used for analysis.

It is noticed that the national food safety standards are set for *i*-As content in rice. Generally, As in rice mainly exists as As(III), As(V), DMA and MMA. In the study, the distribution of total As in different chemical species in rice samples collected from Yingtan was investigated. The results suggested that As in the rice sample was mainly found as As(III) (53.8%), As(V) (23.1%) and DMA (22.1%), while MMA was undetectable. The percentage of inorganic arsenic in rice was 76.9% on average. This result indicated that *i*-As was the dominant form in rice, which was consistent with the results of other studies. It has been reported that the percentage of *i*-As in rice from different provinces in China ranged from 35 to 92%, with a mean value of 69% and a median value of 71% [52]. The percentage of *i*-As in rice from Guangdong, a province located in Southern China, was 87.3% [53]. Thus, the ratio (76.9%) was used to compute the *i*-As contents in rice based on the measured total content of As for further analysis.

3.2. Health Risk Assessment

The HQ for each investigated heavy metal, as well as HI for multiple elements, were calculated for adults and children in the study area. The HI values for adults and children resulting from exposure to soil (Figure 3a) were 0.082 and 0.334, respectively, which were below the acceptable limit of 1. The HI values of dietary intake of rice (Figure 3b) were 4.26 and 5.25 for adults and children, respectively, suggesting that rice consumption could introduce severe non-carcinogenic risks to local residents. Due to the significant variabilities in the measured contents of trace elements in soil and rice samples, considerable uncertainty existed in the estimated risks. In the study, the cumulative probability distributions of HI for local residents were calculated using the log-normal fitting model to account for the uncertainties in metal contents. The results (Figure 3c) showed that the non-carcinogenic risks resulting from the exposure to soil were less than 1 for both adults and children, while those contributed by dietary intake of rice were greater than 1 for almost all residents. Although having lower daily rice intake than adults, children may face higher risks due to their smaller weights. The contributions of non-carcinogenic risks from various elements followed the order of *i*-As > Cd > Cu > Pb > Ni > Cr. Thus, the non-carcinogenic risks were mainly contributed by dietary consumption of rice, and *i*-As and Cd exposure accounted for the majority of the risks. The results were consistent with previous studies in China and Asia [54,55].

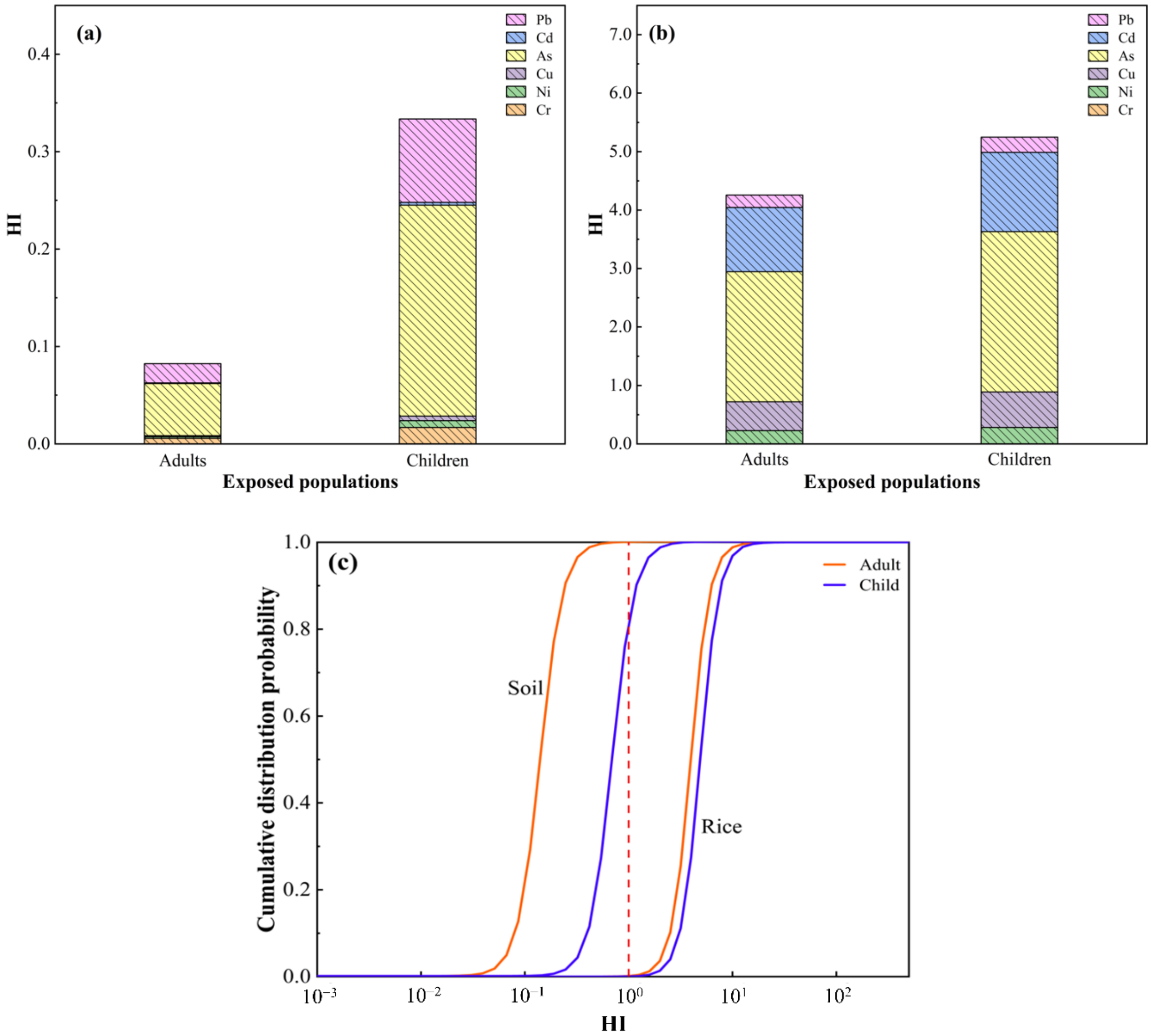

Figure 3. Non-carcinogenic risk contributed by investigated heavy metals: (**a**) estimated HI from exposure to soil; (**b**) estimated HI from exposure to rice; (**c**) cumulative probability distributions of HI.

The ILCR results from oral ingestion, dermal contact and inhalation were calculated and shown in Table 3. The estimated ILCR values of long-term dietary exposure to *i*-As in rice were much higher than 1×10^{-4} for both adults and children, indicating significant carcinogenic risks of bladder and lung cancer, as well as skin cancer, through consuming locally produced rice in the region. Pb basically did not pose significant cancerogenic risks to human beings, with all the ILCR values within the acceptable level. The cumulative probability distributions of ILCR are presented in Figure 4. As shown in the plots, rice consumption posed severe threats to almost all residents in the study area, while the risks resulting from dermal contact and inhalation of soils were neglectable. As expected, *i*-As in rice posed significant carcinogenic health risks, with the additional lifetime risk for both skin cancer and bladder and lung cancer larger than 10^{-4}. In comparison, the cancer risks resulting from exposure to Pb and Cd in rice and soil were much lower, with ILCR values less than10^{-4} for the entire population in the study area.

Table 3. Estimations of carcinogenic risks caused by heavy metals in rice grain and soil.

Item	Exposure Pathway	Heavy Metal	Type of Cancer	ILCR-Adult	ILCR-Child
Rice	Oral ingestion	*i*-As	skin cancer	1.00×10^{-3}	1.23×10^{-3}
		i-As	bladder and lung cancer	1.48×10^{-2}	1.82×10^{-2}
		Pb	liver cancer	6.27×10^{-6}	7.73×10^{-6}
Soil	Oral ingestion	*i*-As	skin cancer	1.86×10^{-5}	8.09×10^{-5}
		i-As	bladder and lung cancer	2.74×10^{-4}	1.19×10^{-3}
		Pb	liver cancer	5.76×10^{-7}	2.50×10^{-6}
	Dermal contact	*i*-As	skin cancer	5.44×10^{-6}	1.66×10^{-5}
	Inhalation	*i*-As	lung cancer	2.20×10^{-8}	2.28×10^{-8}
		Cd	lung and kidney cancer	3.78×10^{-10}	3.90×10^{-10}

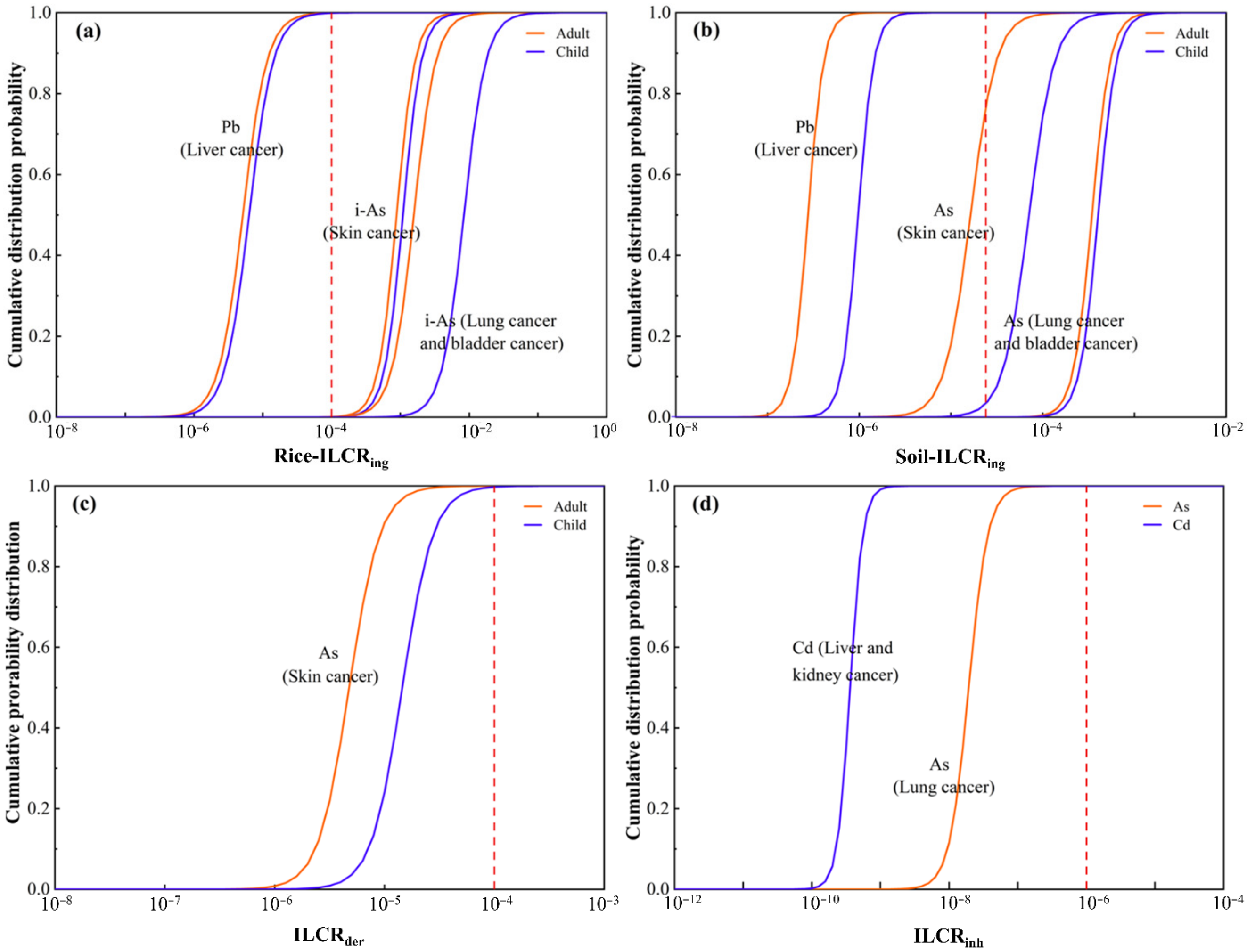

Figure 4. Cumulative probability of incremental lifetime cancer risks for residents resulting from (**a**) oral ingestion of rice; (**b**) oral ingestion of soil; (**c**) dermal contact of soil; (**d**) inhalation of soil.

In summary, the results suggested that consuming locally produced rice can pose serious threats to residents in the study area, especially to children. In particular, *i*-As and Cd in rice contributed significant carcinogenic and non-carcinogenic health risks and require high priority for policymaking.

3.3. Transfer of Heavy Metals from Paddy Soil to Rice

Figure 5 shows the boxplots of $BCF_{rice/soil}$ and $BCF_{husk/soil}$ in the study area, which can be used to evaluate the potential ability of heavy metals to transfer from soil to the edible part of paddy rice. Generally, the mean BCF values of various heavy metals followed the order of Cd > Cu > Ni > As > Cr > Pb in rice grain and the order of Cd > Cu > As > Ni > Pb > Cr in rice husks. The results consistently showed that Cd was the element most likely to accumulate in rice, which is consistent with previous studies [30]. Although the BCF values of Cu and Ni were higher than As, Cr and Pb in rice grain, their potential health risks were relatively low. In contrast, As, having a relatively low mean BCF value of 0.031, could pose significant risks to human beings due to its high toxicity. Cr and Pb had the lowest BCF values due to the fact that these two elements exist mainly in the iron and manganese oxides bounded forms and residual fractions and have low bioavailability [56].

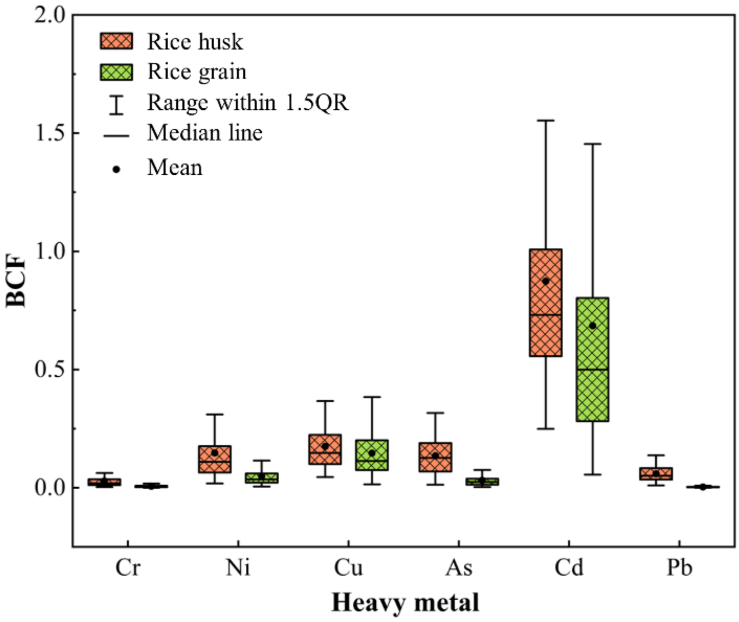

Figure 5. Boxplots of bioconcentration factors for rice grain (BCFrice/soil) and rice husk (BCFhusk/soil) in the study area.

A correlation analysis was performed to investigate the relationships between $BCF_{rice/soil}$ and different impact factors. According to the correlation coefficients (Table 4), the bioavailable fractions of heavy metals in the soil played a critical role in the bioaccumulation process in the soil–rice system, with all the BCF values except Cu having positive and significant correlations with percentages of F1, F1+F2 or F1+F2+F3 obtained by the modified BCR sequential extraction method. In general, F1 included weakly absorbed metals that were considered as the most bioavailable, while F2 and F3 were associated with oxides, carbonates and organic matter contents, which can be potentially bioavailable. It was noteworthy that the mineral elements in the soil were also critical for heavy metal migrations, with the fact that all the BCFs had significant and negative correlations with Al, Mn or Fe contents. Numerous studies have shown that these elements have hindering effects on the migration of heavy metals. Iron and manganese oxides may play dominant roles in adsorbing heavy metals [57] and have been used to immobilize exchangeable heavy metals in soil [58,59]. Soil pH and TOC are important impacting factors on the distribution, migration and transformation of heavy metals. The paddy soil samples collected in Yingtan had pH values ranging from 4.26 to 6.69, with a mean of 5.00, indicating acidic conditions throughout the region. Soil pH usually affects metal mobility and bioavailability through adsorption and desorption. In general, a lower pH could increase the solubility and mobility of heavy metals, such as Cd, Cu and Pb, and enhance their transfer from soils to crops [28,31], while a higher pH would facilitate the release of As from soil minerals [60]. The low pH of acidic red soil may result in the accumulation of heavy metals in rice grown in uncontaminated soils [61]. In the study, increasing soil acidity would facilitate the migrations of Cu, As and Cd from soil to rice, whereas it had little impact on Cr, Ni and Pb. The BCF of As had a negative correlation with the soil pH, which was different from the crops and vegetables grown in the uplands [62,63]. This could be attributed to the change in pH during the booting stage of rice growth, which plays a critical role in uptaking As from soil to the plants. Under flooded conditions, soil pH would increase from the original value to approximately 7.0 [64]. In the study area, the soil TOC values ranged from 3.90 to 29.1 mg/kg, with a mean value of 14.6 and a standard deviation of 6.05 mg/kg, suggesting significant variations in TOC contents in the paddy soils. It was found that the TOC contents had positive and significant correlations to the BCFs of Cu and As. High TOC contents in the soil may indicate the accumulation of humus, which can retain heavy metals in exchangeable forms and increase their availability to plants [24]. In addition, organic matter might compete with As for binding sites and lead to high As bioavailability in soils [65].

Table 4. Correlation coefficients between BCFrice/soil and different impact factors.

Impact Factor	Bioconcentration Factor					
	Cr	**Ni**	**Cu**	**As**	**Cd**	**Pb**
F1	0.144	−0.112	−0.343 *	0.258	0.394 *	0.058
F1 + F2	0.386 **	0.260 *	0.129	0.336 *	0.485 **	0.408 **
F1 + F2 + F3	0.280 *	0.023	0.208	0.422 **	0.483 **	0.351 *
TOC	0.008	0.056	0.329 *	0.258 *	0.202	−0.089
pH	0.023	0.16	−0.251 *	−0.307 *	−0.344 *	−0.092
Al	−0.075	−0.148	−0.287 *	−0.287 *	0.113	0.033
Mn	−0.172	−0.397 **	−0.139	0.014	−0.423 **	−0.480 **
Fe	−0.386 *	−0.141	−0.068	−0.115	−0.306 *	−0.019

Note: ** represents significant correlation at the level of 0.01; * represents significant correlation at the level of 0.05; F1, F2 and F3 represent the acid-extractable, reducible and oxidable and residual fraction obtained by the modified BCR continuous extraction method, respectively.

Stepwise regressions were used to construct multiple linear regression models. As shown in Table 5, the fitted empirical models had R^2 values ranging from 0.166 for Cu to 0.435 for Cd and all p-values less than 0.05, indicating that they were effective to predict the bioaccumulation behavior of the heavy metals. In particular, the results revealed that acid-extractable Cd in soils, soil pH and Mn contents were the most important controlling factors in explaining the BCF of Cd, while the transfer of As from soil to rice could be efficiently predicted by its non-residual fractions in soils and soil pH. High bioavailable fractions and low soil pH would enhance the accumulation of Cd and As in rice, which may help to set effective pollution prevention and control policies in the study area. However, further investigation is required to improve the model performance, especially for As. More work is needed to understand the migration mechanism of various heavy metals in the soil–rice system and to accurately identify the main influencing factors.

Table 5. Multivariate linear regression models for $BCF_{rice/soil}$ obtained by stepwise regression method.

Heavy Metal	Fitted Equation	R^2	p-Value
Cr	$\text{Log(BCF)} = -0.630 + \log(\text{Cr}_{F1}) - 0.527 \log(\text{Fe})$	0.295	<0.01
Ni	$\text{Log(BCF)} = -0.655 + 0.292 \log(\text{Ni}_{F1}) - 0.458 \log(\text{Mn})$	0.206	<0.01
Cu	$\text{Log(BCF)} = -0.664 + 0.671 \log(\text{TOC}) - 0.236 \log(\text{Al})$	0.166	<0.05
As	$\log(\text{BCF}) = -1.594 + 3.305 \log(\text{As}_{F1+F2+F3}) - 1.902 \log(\text{pH})$	0.237	<0.01
Cd	$\text{Log(BCF)} = -1.868 + 1.841 \log(\text{Cd}_{F1}) -1.483\log(\text{pH}) - 0.482 \log(\text{Mn})$	0.435	<0.01
Pb	$\log(\text{BCF}) = -2.426 + 0.397 \log(\text{Pb}_{F1}) - 0.369 \log(\text{Mn})$	0.319	<0.01

4. Conclusions

The contents of heavy metals in soils and rice in Yingtan were investigated. The results showed that the paddy fields had been severely impacted by human activities, and consuming locally produced rice posed significant health risks to local residents. As and Cd were the major pollutants in the study area, and dietary intake of rice is the dominant exposure pathway leading to the carcinogenic and non-carcinogenic risks. The correlation coefficients and the stepwise multiple linear models suggested that the enrichment of As and Cd in rice was mainly controlled by their contents in bioavailable fractions in soils, soil pH and mineral element Mn. The concentrations of Cd and As in rice grains were negatively correlated with the soil pH values, indicating that low pH can enhance their bioaccumulation behaviors. The presence of element Mn could inhibit the migration of Cd from soils to rice grains to some extent.

The study provided a comprehensive understanding of heavy metal pollution in soils and rice as well as the health risks faced by local residents due to their exposure to heavy metals through multiple pathways. In addition, the potential controlling factors for the transfer of toxic metals from soils to rice grains were identified, and the models for predicting their bioaccumulation behaviors in the soil–rice system were constructed. The findings can effectively support the policymaking for food safety and human health protection. Based on the identified major pollutants and pathways leading to high health risks, policymakers can formulate low-cost and high-efficiency pollution prevention and control regulations in a targeted manner. According to the results of the constructed predictive models, practical soil remediation measures would be developed to reduce the migration of heavy metals from soil to rice. The work suggests that it is critical to further investigate the migration mechanisms of the heavy metals in soil–rice systems under various field conditions, and more soil properties and plant functions should be considered for accurately predicting their enrichment patterns. To ensure the safety of soil for agricultural production, a simple value based on the total amount of the toxic metal may not be appropriate, especially for As. More work is required to develop suitable soil quality criteria based on the bioavailable fractions of the heavy metals, pH conditions and other critical controlling factors.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su141610225/s1, Figure S1: The image of plasma-mass spectrometer (ICP-MS, NexION 350D, PerkinElmer, Waltham, MA, USA); Table S1: The values of the exposure parameters [39,66–71]; Table S2: Reference values of RfD and CSF of heavy metals through different exposure pathways [72–78].

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Abbreviations

ADI	Average Daily Intake
BCF	Bioconcentration Factor
DMA	Dimethylarsine
GDP	Gross Domestic Product
HI	Hazard Index
HQ	Hazard Quotient
ILCR	Incremental Lifetime Cancer Risk
MMA	Monomethylarsine
TOC	Total Organic Carbon
QA	Quality Assurance
QC	Quality Control
USEPA	U.S. Environmental Protection Agency

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