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# A Case Study: Arsenic, Cadmium and Copper Distribution in the Soil–Rice System in Two Main Rice-Producing Provinces in China

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**Abstract:** Arsenic (As) and cadmium (Cd) pose great risk to rice plants and human health. Copper (Cu) agrichemicals also draw increasing attention. This study investigated the distributions of As, Cd and Cu in the soil–rice system in two major rice-producing provinces, Hunan and Jiangxi, China. Arsenic in soils at site A in Hunan reached 47.95–60.25 mg/kg, all exceeding the national standard (GB15618-2018), but As in rice was all below the safe limit for humans (0.20 mg/kg, GB2762-2017). In contrast, As in all rice husks and 5% of grain samples from Jiangxi exceeded the safe limit, while As in soils was 3.40–9.92 mg/kg, all below the standard. Cadmium in soils at site A and site B in Hunan were 3.96–5.11 and 1.83–2.77 mg/kg, respectively, all exceeding the national standard; Cd in 60% of rice grains exceeded the safe limit (0.20 mg/kg, GB2762-2017). Despite Cd in soils from Jiangxi being much lower (0.20–0.34 mg/kg), Cd in 56% of the rice grains exceeded the safe limit. The different distribution patterns of As and Cd in the soil–rice system probably result from the dynamic environmental conditions during farming practice. Risk from dietary products made from rice husks should also be considered. Although not regulated in rice, Cu in the soil from Hunan exceeds the national standard. This study helps to understand As and Cd pollution in paddies and its risk to human health, and suggests limiting the application of Cu-based agrichemicals.

**Keywords:** heavy metal; agriculture; rice; byproduct; human health

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**Citation:** Liu, J.; Su, J.; Wang, J.; Song, X.; Wang, H. A Case Study: Arsenic, Cadmium and Copper Distribution in the Soil–Rice System in Two Main Rice-Producing Provinces in China. *Sustainability* **2022**, *14*, 14355. https://doi.org/10.3390/su142114355

Academic Editor: Shibao Chen

Received: 7 October 2022
Accepted: 1 November 2022
Published: 2 November 2022

## 1. Introduction

Heavy metal (HM) pollution in agricultural soil caused by mining, industries and conventional agricultural practice is becoming increasingly evident, which has threatened food security and human health. Arsenic (As) and cadmium (Cd) have been shown to be two primary HMs causing soil pollution in China, and have polluted 2.7% and 7.0% of the surveyed soils according to their environmental quality standards for soil in China, respectively [1]. Rice plants are more likely to enrich As and Cd than other food crops, because of their special living environment and unique physiological characteristics [2–4]. Being the staple food for over half of the world's population, rice is the major source of As and Cd in humans in addition to drinking water, thus becoming the major chronic exposure route affecting human health via diet [5,6].

Both inorganic arsenic (iAs) and Cd are classified as Group I carcinogens by the International Agency for Cancer (IARC) [7]; As and Cd rank first and seventh on the Priority List of Hazardous Substances released by US Agency for Toxic Substances and Disease Registry (ATSDR) [8]. Therefore, limit values for iAs and Cd in rice and rice products for young children were proposed by international organizations: limits for iAs are 200 μg/kg polished rice (350 μg/kg brown rice) and 100 μg/kg, respectively [9,10]; limits for Cd are 150 and 40 μg/kg, respectively [11]. China has tentatively set a unified limit value for iAs and Cd in rice, which is 200 μg/kg (GB2762–2017) [12]. By this standard, about 50,000 tons of rice in China is contaminated with Cd each year, with a concentration of up to 7000 μg/kg [13]. The average Cd concentration in rice produced in some areas of southern China reached 330–690 μg/kg (40,263 samples), and about 56%–87% of the samples exceeded the national standard [14]. These concentrations were quite close to or even higher than the average Cd concentration of rice (380 μg/kg) produced in the Jintong River Basin of Japan, where the "itai-itai disease" was first diagnosed in humans in 1931. Therefore, it is urgent to take measures to reduce Cd intake by local people who have Cd-contaminated rice as their staple food. In addition, the average As content was 16–310 μg/kg (6078 samples) in rice from major rice-producing areas in China, i.e., northeast, reaches of Yellow–Huang–Huai rivers, and the middle and lower reaches of Yangzi River, and 10.3% of the samples exceeded the national standard [15]. Similar to Cd, As pollution in rice is also regionalized, and the risks cannot be ignored, especially to local populations. Particularly, As and Cd can be co-enriched in rice grains and exert joint effects to the human body, which significantly increases the health risk [16]. Furthermore, as an important byproduct of rice cultivation, husks have also been used in dietary products, which pose additional risk to humans since husks normally accumulate more As than the grains [17,18]. According to monitoring by the China Ecosystem Research Network (CERN) from 2005 to 2017, the concentrations of As and Cd in paddy soils in some areas of China are still on the rise [19]. However, due to China's large population and limited land resources, it is still necessary to use moderately and slightly polluted farmland to produce food. Therefore, it is critical to remediate polluted farmland to reduce the accumulation of As and Cd in rice and ensure food security, which is closely related to the national economy and people's livelihood. In addition, Cu-based agrichemicals and nanomaterials, topics in recent research literature, may be related to the transport of other components (such as As and Cd) in rice plants [20–26]. Although no limit has been set for Cu concentration in rice or other food products, many countries and organizations have established the standard for Cu in the soil [27].

Hunan and Jiangxi ranked the second and third in rice-producing provinces in China, producing 26.4 and 20.5 million tons of rice in 2021, respectively [28]. Additionally, rich mineral resources in the two provinces have boosted the development of heavy industries and caused serious HM pollution in agricultural soil and irrigation water [14,15,29]. There have been many case studies on rice pollution near industrial sites in the two provinces. In this study, the sampling paddies were randomly chosen relatively far (>5 km) from large-scale industrial sites in order to understand the status quo of soil pollution by As, Cd and Cu with little industrial influence and their accumulation in rice grains and potential health risk to humans.

## 2. Materials and Methods

### 2.1. Sampling

Paired soil and rice samples were collected from two conventional paddies in each of the two main rice-producing provinces, Hunan (HN) and Jiangxi (JX), in 2021 (HN-A, HN-B, JX-A and JX-B, Figure 1). Rice cultivars (*Oryza sativa*) were 215,595 superior rice and Changshengyou 989 grown in the chosen paddies in Hunan and Jiangxi. Five sampling points with an S-shaped distribution were chosen in each paddy; a soil cone with a depth of 20 cm and rice plants at the mature stage were collected as a pair from each sampling point (Figure 2).

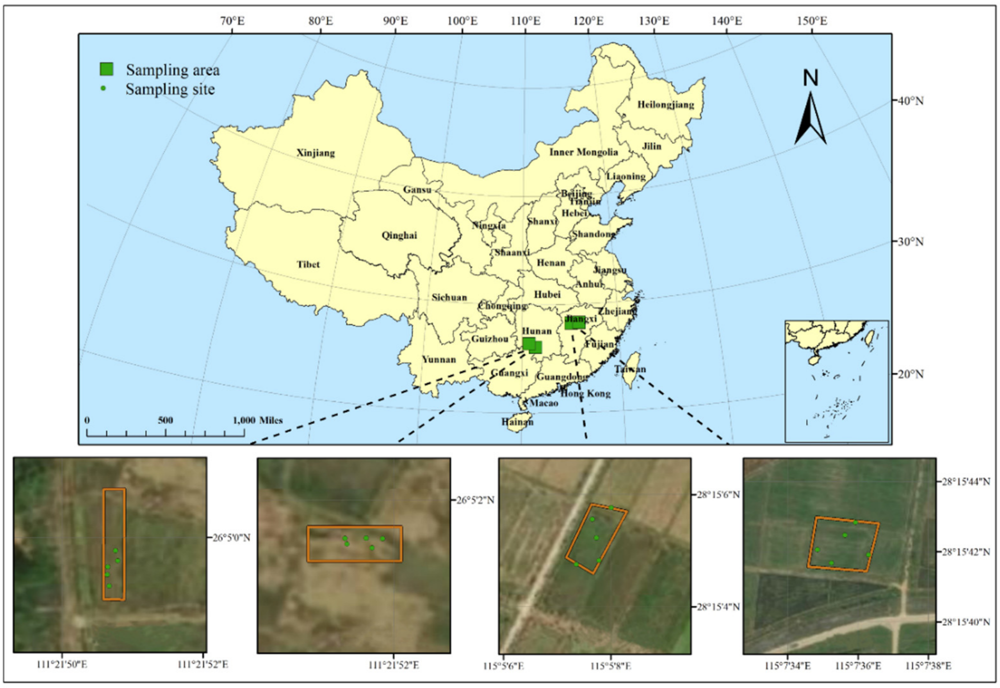


**Figure 1.** Geographical information for the four sampling sites in Hunan and Jiangxi provinces, China (from left to right: HN-A, HN-B, JX-A and JX-B).

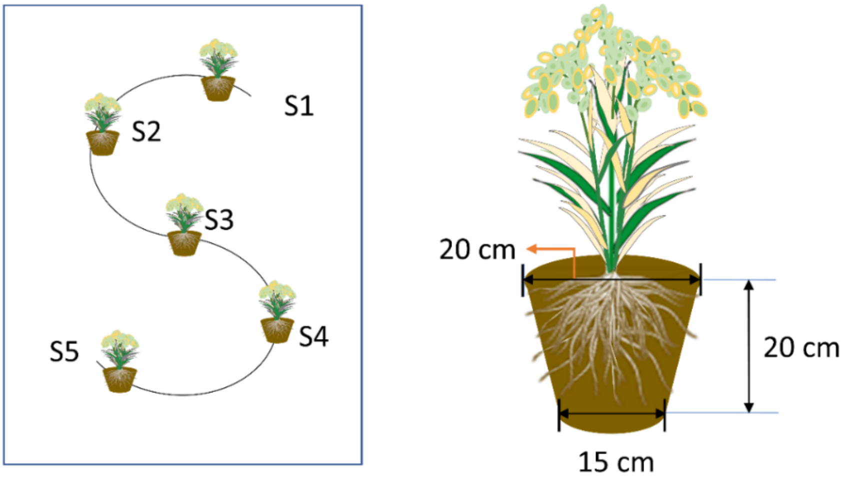


**Figure 2.** Sampling point distribution in a chosen paddy (**left**) and description of soil cone and rice plants (**right**).

## 2.2. Chemical Analyses

Rice grains were collected and dried in an oven at 45 °C. Duplicate rice grain samples with 10 grains for each replicate were digested with $HNO_3$ and $H_2O_2$ using a heat block for each sampling point using a procedure adapted from the USEPA 3050B method [30]. Rice grain samples were separated into husks and dehusked grains, and digested separately for chemical analysis. Soil samples were air-dried and sieved through a 1 mm mesh. Duplicate soil samples at each sampling site were dried in the oven at 60 °C for 48 h and weighed (about 0.5 g) for digestion. Soils for As measurement were digested with HCl and $HNO_3$ (3:1) using a microwave digestion system (HJ 680-2013); soils for Cd and Cu measurement were digested with HCl and $HNO_3$ (3:1) using a heating block (HJ 803-2016). Standard references materials consisting of rice (GBW10010a) and soil (GBW07386(GSS-30)) were digested together with the samples. All the digestates of rice and soil were measured for concentrations of As with atomic fluorescence spectrometry (AFS, PF52) and Cd and Cu with an inductively coupled plasma mass spectrometer (ICP-MS, iCAPRQ). The detection limits for As, Cd and Cu were 0.06, 0.07 and 0.5 mg/kg, respectively. The recovery rate of the elements measured in the standard references materials were controlled within the range 100 ± 20%. Other physicochemical properties of soils were determined, including the texture of soils, pH, cation exchange capacity (CEC) (LY/T 1243-1999), available phosphorus (P) (HJ 704-2014), available potassium (K) (NY/T 1849-2010), total nitrogen (TN) (HJ717-2014) and organic matter (OM) (NY/T 1121.6-2006).

### 2.3. Statistical Analyses

Generalized linear models (GLMs) were used to compare the differences in soil properties and HM concentrations in the samples from the four sites in the two provinces, as well as to evaluate the effect of soil properties on HM uptake in rice. Data distributions were defined in the model. Models were validated and accepted with low residual heterogeneity, followed by an analysis of variance (ANOVA). Data were expressed as means ± S.E.M (standard error of measurement). Means were considered significantly different when $p < 0.05$ with the Tukey HSD test. All statistical analyses and associated figures were performed in R (version 4.2.1) [31].

## 3. Results and Discussion

Fundamental physicochemical properties of soil samples from rice paddies in Hunan and Jiangxi are shown in Table 1. The soil texture from the four sites was classified as clay. There was no significant difference in CEC, P or inorganic anions of soils from the two provinces, while the CEC of soils from the two sites in Jiangxi showed significant difference. Significant differences in K and TN were observed in soils from at least one pair of sampling sites from the two provinces. Particularly, the pH and OM in the soil from the four sites were significantly different. These differences, especially pH and OM, contributed to the variance of HM concentrations in the rice samples from the paired soil sampling sites in the two provinces.

**Table 1.** Fundamental physicochemical properties of soil samples from four rice paddies in Hunan (HN) and Jiangxi (JX) provinces.

| Sampling Sites | Sampling Point | CEC [a] (cmol/kg) | Available P [b] (mg/kg) | Available K [c] (mg/kg) | Total N [d] (mg/kg) | Organic Matter (g/kg) | Inorganic Anions (mg/L) | pH |
|---|---|---|---|---|---|---|---|---|
| HN-A | Soil 1 | 7.2 ± 0.30 | 13.0 ± 0.45 | 9.0 ± 0.11 | 129.5 ± 1.5 | 9.9 ± 1.8 | 17.2 ± 0.35 | 5.9 ± 0.1 |
| | Soil 2 | 7.3 ± 0.05 | 12.9 ± 0.20 | 9.0 ± 0.16 | 126.5 ± 7.5 | 12.3 ± 0.4 | 15.8 ± 0.15 | |
| | Soil 3 | 7.3 ± 0.20 | 12.8 ± 0.30 | 9.0 ± 0.13 | 157.5 ± 0.5 | 14.8 ± 0.2 | 15.5 ± 0.30 | |
| | Soil 4 | 7.7 ± 0.10 | 12.6 ± 0.00 | 8.9 ± 0.04 | 156.0 ± 2.0 | 20.1 ± 0.3 | 15.9 ± 0.55 | |
| | Soil 5 | 7.6 ± 0.10 | 12.4 ± 0.05 | 9.2 ± 0.01 | 152.0 ± 3.0 | 20.6 ± 1.3 | 15.5 ± 0.35 | |
| HN-B | Soil 1 | 7.9 ± 0.45 | 12.5 ± 0.05 | 9.0 ± 0.11 | 150.5 ± 2.5 | 33.7 ± 0.7 | 15.6 ± 0.65 | 5.4 ± 0.1 |
| | Soil 2 | 7.6 ± 0.05 | 12.7 ± 0.10 | 8.9 ± 0.05 | 153.0 ± 1.0 | 40.0 ± 0.7 | 15.6 ± 0.35 | |
| | Soil 3 | 7.4 ± 0.05 | 12.3 ± 0.10 | 9.0 ± 0.05 | 143.0 ± 5.0 | 39.1 ± 0.9 | 15.0 ± 0.20 | |
| | Soil 4 | 7.4 ± 0.20 | 12.6 ± 0.05 | 9.0 ± 0.02 | 156.0 ± 5.0 | 45.3 ± 0.1 | 15.1 ± 0.25 | |
| | Soil 5 | 7.5 ± 0.05 | 12.5 ± 0.35 | 8.9 ± 0.10 | 154.5 ± 2.5 | 49.9 ± 1.4 | 15.0 ± 0.40 | |
| JX-A | Soil 1 | 7.0 ± 0.15 | 13.7 ± 0.05 | 10.6 ± 0.15 | 155.0 ± 3.0 | 29.9 ± 0.7 | 14.0 ± 0.15 | 5.0 ± 0.1 |
| | Soil 2 | 6.8 ± 0.25 | 12.6 ± 0.20 | 9.6 ± 0.32 | 164.0 ± 3.0 | 31.8 ± 0.3 | 15.1 ± 2.15 | |
| | Soil 3 | 7.5 ± 0.30 | 12.0 ± 0.10 | 10.9 ± 0.05 | 163.5 ± 4.5 | 28.4 ± 3.6 | 17.1 ± 0.90 | |
| | Soil 4 | 7.1 ± 0.15 | 13.2 ± 0.05 | 11.2 ± 0.25 | 152.5 ± 0.5 | 30.7 ± 0.1 | 15.6 ± 0.05 | |
| | Soil 5 | 7.6 ± 0.05 | 12.5 ± 0.25 | 9.5 ± 0.10 | 126.5 ± 1.5 | 31.5 ± 0.4 | 15.5 ± 0.60 | |
| JX-B | Soil 1 | 7.7 ± 0.10 | 13.0 ± 0.15 | 8.8 ± 0.02 | 111.0 ± 2.0 | 23.9 ± 1.0 | 15.1 ± 0.65 | 5.2 ± 0.0 |
| | Soil 2 | 7.0 ± 0.15 | 12.4 ± 0.15 | 9.2 ± 0.04 | 125.5 ± 1.5 | 25.2 ± 1.9 | 14.8 ± 2.20 | |
| | Soil 3 | 8.3 ± 0.10 | 12.6 ± 0.05 | 9.3 ± 0.02 | 143.5 ± 7.5 | 26.8 ± 1.6 | 16.3 ± 0.10 | |
| | Soil 4 | 7.8 ± 0.35 | 13.0 ± 0.15 | 8.7 ± 0.12 | 152.5 ± 5.5 | 21.8 ± 1.7 | 16.1 ± 0.25 | |
| | Soil 5 | 7.3 ± 0.45 | 13.0 ± 0.30 | 9.0 ± 0.01 | 152.5 ± 3.5 | 20.2 ± 1.1 | 17.4 ± 0.20 | |

**Table 1.** *Cont.*

| **Sampling Sites** | **Sampling Point** | **CEC [a] (cmol/kg)** | **Available P [b] (mg/kg)** | **Available K [c] (mg/kg)** | **Total N [d] (mg/kg)** | **Organic Matter (g/kg)** | **Inorganic Anions (mg/L)** | **pH** |
|---|---|---|---|---|---|---|---|---|
| ∗ **Significant difference** | | JX-A∗JX-B | None | HN-A∗JX-A<br>JX-A∗JX-B | HN-B∗JX-B<br>JX-A∗JX-B | HN-A∗JX-A<br>HN-B∗JX-B<br>HN-A∗HN-B<br>JX-A∗JX-B | None | HN-A∗JX-A<br>HN-A∗HN-B |

**Texture of soils**

| | **HN-A** | **HN-B** | **JX-A** | **JX-B** |
|---|---|---|---|---|
| Silt (%) | 3.83 ± 0.10 | 3.77 ± 0.16 | 3.13 ± 0.16 | 3.61 ± 0.17 |
| Sand (%) | 9.68 ± 0.14 | 9.05 ± 0.16 | 7.70 ± 0.23 | 9.94 ± 0.24 |
| Clay (%) | 86.53 ± 0.14 | 87.18 ± 0.24 | 89.17 ± 0.32 | 86.45 ± 0.40 |
| Texture [e] | Clay | Clay | Clay | Clay |

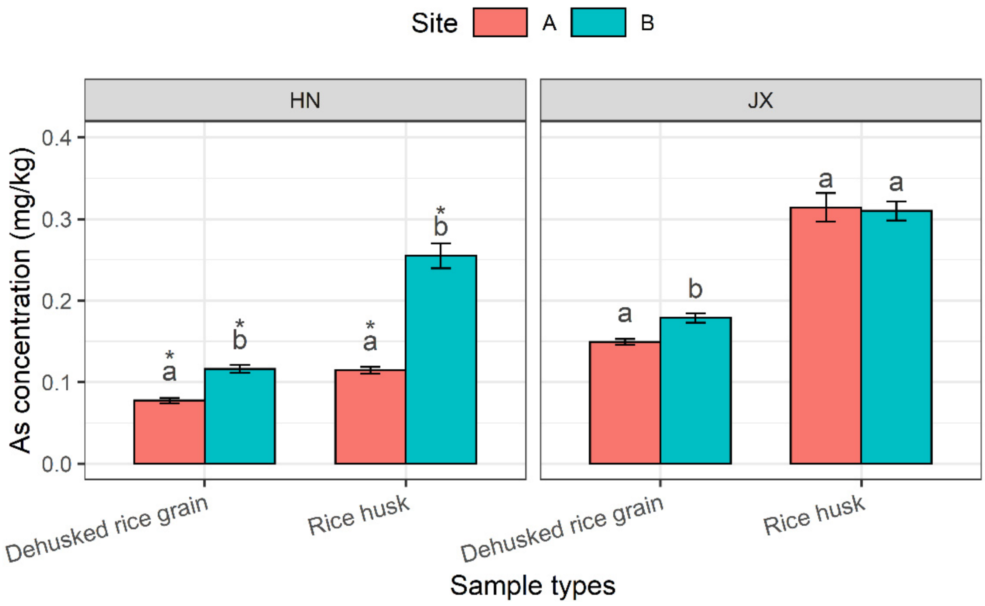
Note: [a] CEC—cation exchange capacity; [b] P—phosphorus; [c] K—potassium; [d] N—nitrogen; [e] type of texture was determined with the online soil texture calculator based on percent silt, sand and clay, developed by the United States Department of Agriculture (https://www.nrcs.usda.gov/wps/portal/nrcs/detail/soils/survey/?cid=nrcs142p2_054167, accessed on 28 August 2022). Data are expressed as means ± S.E.M for duplicate samples at each sampling point, except pH (n = 5 for each site). ∗ indicates the parameter in that column is significantly different between the two sites at $p < 0.05$ level.

Arsenic concentrations in the dehusked rice grains showed significant difference in samples from the two sites in both Hunan and Jiangxi provinces, respectively (Figure 3). In Jiangxi province, As concentrations in dehusked rice grains from JX-A and JX-B averaged 0.149 and 0.179 mg/kg, which were 92.5% and 53.9% higher than those from Hunan province, respectively (Figure 3, Tables 2 and 3). Although these concentrations were lower than the proposed safe limit for iAs in rice in China (GB2762–2017), rice from JX-A and JX-B may pose risk to the younger population, because As in 100% of the dehusked rice grains exceeded the corresponding safe limit for children [9,10]. Although As concentrations were lower in rice samples from Hunan than Jiangxi, there were still 50% of the dehusked rice grains exceeding the proposed safe limit of As for children. Concentrations of As in the husks were significantly higher than those in the dehusked grain, which indicates that husks are the last barrier for As transport into the grains. Arsenic in the husks from JX-A and JX-B were 0.314 and 0.309 mg/kg, which were 174.4% and 21.6% higher than those from HN-A and HN-B, respectively. This comparison is consistent with As concentrations in the dehusked grains from the two provinces. According to the International Rice Research Institute (IRRI), each kilogram of milled white rice will produce 0.28 kg of husks during the milling process [32]. Rice husks have been used in energy generation, building materials, soil fertilizers, litter and bedding materials in poultry houses, animal food additives, pillow stuffing and winemaking [17,18]. When used in animal food additives and dietary products, the high concentrations of As in husks may pose risks to humans and animals.

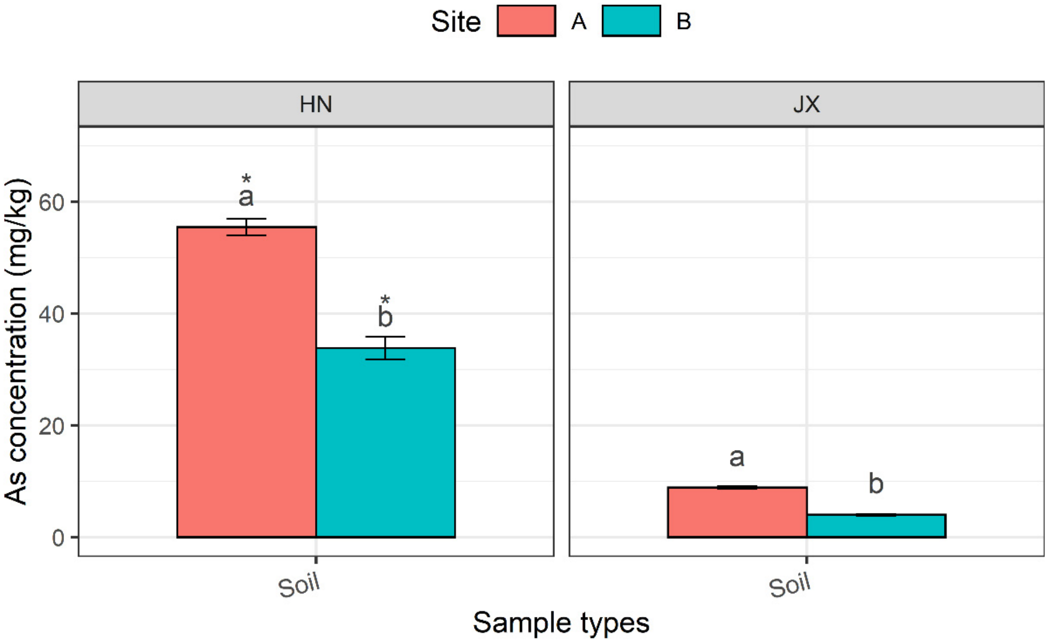
Cadmium concentrations in dehusked rice grains from the two sampling sites in Hunan and Jiangxi provinces were significantly different, averaging 0.354, 0.100, 0.094 and 0.453 mg/kg for samples from HN-A, HN-B, JX-A and JX-B, respectively (Figure 4, Tables 2 and 3). Accumulated Cd in the dehusked grain samples from HN-A and JX-B were all significantly higher than the safe limit (i.e., 0.2 mg/kg), while Cd in 89.5% of all the samples from the four sampling sites exceeded the limit set for infants, i.e., 0.04 mg/kg. Therefore, rice produced from all these sites could cause potential risks to humans, especially to younger populations. Different from dehusked grain samples, Cd concentration in rice husks showed no significant difference in samples from HN-A and HN-B, while it was statistically different in husks from HN-B and JX-B (Figures 3 and 4). Cadmium concentrations in rice husks averaged 0.128, 0.078, 0.081 and 0.155 mg/kg, respectively, for HN-A, HN-B, JX-A and JX-B (Tables 2 and 3). Unlike As distribution in rice, Cd in dehusked grains was higher than in the husk. These results indicate the mechanisms and defense of transport are different for As and Cd.

Arsenic concentrations were 55.46, 33.84, 8.91 and 4.04 mg/kg in the soil from HN-A, HN-B, JX-A and JX-B, respectively, while Cd concentrations in the soil were 4.44, 2.30, 0.22 and 0.30 mg/kg, respectively (Figures 3 and 4, Tables 2 and 3). Specifically, As in 100% and 70% of soil samples from HN-A and HN-B, respectively, exceeded the national standard (30 mg/kg when $pH \leq 6.5$) set for farming soil in China (GB15618-2018) [33]; whereas As in the soil from all of the sampling sites in Jiangxi were 66.0%–88.3% lower than the standard. Additionally, Cd in the soil samples from Hunan exceeded the standard (GB15618-2018, 0.3 mg/kg when $pH \leq 5.5$, and 0.4 mg/kg when $5.5 < pH \leq 6.5$) by 4.5–8.3 and 8.4–12.4 times for HN-A and HN-B, respectively; while Cd was all below the standard in soils from JX-A, and Cd exceeded the standard in 40% of soil samples from JX-B. These results showed that HN-A and HN-B were both severely polluted by As and Cd, while JX-B was slightly polluted by Cd. Given that these sampling sites were little influenced by heavy industries, the pollution can probably be attributed to conventional farming practice or geogenic background, which needs to be further investigated. Additionally, we could not rule out the probability of influence by heavy industries during the long term. Although soils from some of the sampling sites were not heavily polluted, rice products from these sampling sites can still pose risks to certain population groups or animals, since the accumulations of As and Cd in rice grains are not only dependent on their total concentrations in the soil but also to their bioavailable fraction to the plants [4]. Particularly, the bioaccumulation factor of Cd in dehusked rice grains from the soil at JX-B was 1.35–1.84, resulting in the elevated Cd in rice grains, which is higher than the proposed safe limit. This result was probably due to the lower pH and higher organic content (OM) in the soil from JX-B [16]. In addition, As in rice grains from JX was higher than HN, while As in soil samples from JX was much lower than HN; this result also indicates that environmental factors exert more pronounced effect on the bioaccumulation of As by rice plants than As content in the soil. General linear models together with ANOVA analysis proved that As accumulation in rice grains was significantly influenced by pH, TN and OM, in addition to As concentration in the soil; Cd accumulation in rice grains was influenced by CEC, available K and OM, in addition to Cd content in the soil. Rice variety did not show a significant influence on As and Cd accumulation in rice grains. Therefore, As and Cd in the rice grains produced will be lower than the safe limit once proper treatment is adopted to reduce the bioavailability of As and Cd in the soil.

In recent decades, progress has been achieved to understand the geochemical cycling and translocation of As and Cd from soil to plants [34–36]. Environmental factors influencing HM bioavailability in the soil include pH, redox state (Eh), ECE, P, OM, salinity, microbial activity and other components, as shown in Table 1 [37–39]. The process of activation and dissolution of As/Cd from the adsorption state on the surface of soil particles and migration to the rice root surface is crucial to determining their bioavailability. This process is related to soil OM, mineral components and functional microbial activity, etc., and is affected by soil pH and Eh [16]. Soil OM can provide adsorption sites for As/Cd and reduce its mobility, which explains the lower accumulation of As in rice sampled from JX-A than JX-B, although the As content in the soil was higher at JX-A. Minerals in the soil, especially iron-containing minerals, also prevent or mediate the entry of As/Cd into plants since they can form an iron plaque on the soil and the plant root surface [16]. In addition to directly participating in the species transformation of As and Cd, soil microorganisms also affect the soil environment by secreting organic acids and extracellular enzymes, and degrading organic matter, thereby indirectly affecting the speciation and bioavailability of As and Cd [22,40]. Furthermore, As and Cd behave differently under the influence of pH–Eh [16,41–43]. When the pH is low, Cd is dissociated from soil particles and exists in an ionic state ($Cd^{2+}$) or complex ion state ($Cd(NH_3)^+$, $Cd(CN)^+$, $CdCl^+$); When the pH is high, soil particles are negatively charged and adsorb $Cd^{2+}$, and insoluble salts such as $Cd_3(PO_4)_2$ also form to precipitate $Cd^{2+}$ from the solution [41]. In addition, Cd is more available in aerobic (high Eh) soils than in anaerobic (low Eh) soils due to the formation of insoluble CdS in reductive condition [44]. Being able to exist in variable valence states, As is more affected by pH and Eh [41]. The increase in pH and the decrease in Eh lead to the increase in water-soluble As content due to desorption of As from soil particles and reduction of As(V) to As(III), thereby increasing the bioavailability of As [16]. Regulating the pH–Eh relationship of the environment is used to balance the bioavailability of Cd and As, which is a difficulty in general water and fertilizer management, and a challenge in developing new technologies to simultaneously passivate the migration of Cd and As in the environment.



(**a**)



(**b**)

**Figure 3.** Arsenic (As) concentrations in the paired dehusked rice grain, rice husk (**a**) and soil samples (**b**) from two sampling sites in Hunan (HN) and Jiangxi (JX) provinces; lower-case letter indicates a significant difference ($p < 0.05$) between two sites in the same province, while the * symbol presents the differences ($p < 0.05$) at two sites across the two provinces.

**Table 2.** Concentrations (mg/kg) of arsenic (As), cadmium (Cd) and copper (Cu) in the samples from Hunan province (HN).

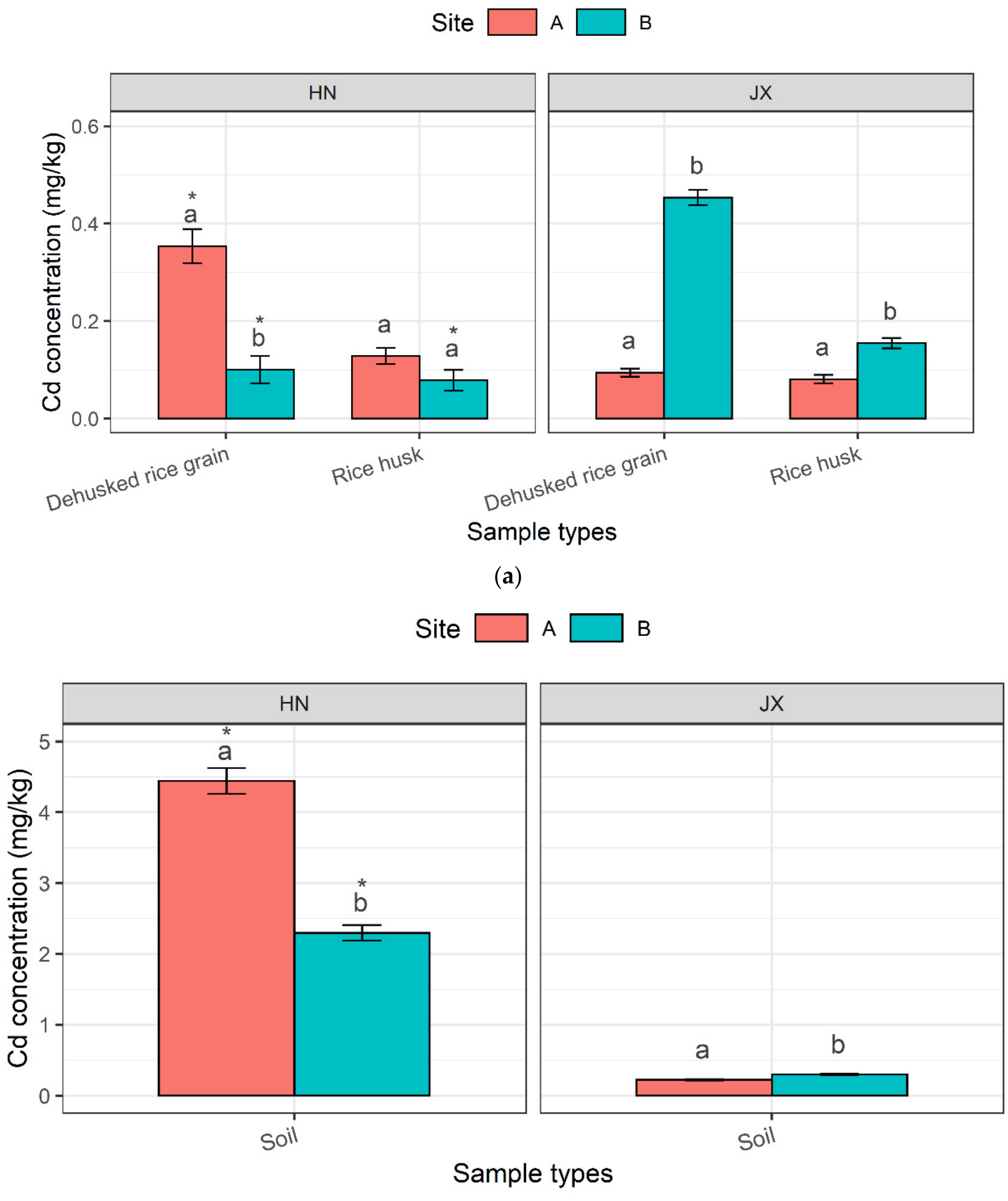
| Sampling Sites | Sample Id | As (mg/kg) | Cd (mg/kg) | Cu (mg/kg) |
|---|---|---|---|---|
| HN-A | Dehusked rice grain S1 | 0.076 ± 0.003 | 0.302 ± 0.003 | 3.08 ± 0.192 |
| | Dehusked rice grain S2 | 0.091 ± 0.004 | 0.389 ± 0.029 | 3.04 ± 0.076 |
| | Dehusked rice grain S3 | 0.076 ± 0.007 | 0.352 ± 0.000 | 2.85 ± 0.040 |
| | Dehusked rice grain S4 | 0.063 ± 0.002 | 0.205 ± 0.010 | 2.33 ± 0.018 |
| | Dehusked rice grain S5 | 0.081 ± 0.000 | 0.522 ± 0.012 | 2.44 ± 0.150 |
| | Rice husk S1 | 0.107 ± 0.008 | 0.116 ± 0.034 | 2.68 ± 0.018 |
| | Rice husk S2 | 0.127 ± 0.005 | 0.111 ± 0.014 | 2.65 ± 0.205 |
| | Rice husk S3 | 0.103 ± 0.005 | 0.176 ± 0.083 | 2.43 ± 0.160 |
| | Rice husk S4 | 0.108 ± 0.004 | 0.096 ± 0.022 | 2.41 ± 0.072 |
| | Rice husk S5 | 0.128 ± 0.003 | 0.141 ± 0.007 | 1.86 ± 0.127 |
| | Soil 1 | 60.25 ± 0.65 | 5.11 ± 0.25 | 62.80 ± 3.50 |
| | Soil 2 | 55.85 ± 0.15 | 4.92 ± 0.44 | 62.70 ± 1.320 |
| | Soil 3 | 56.25 ± 0.45 | 4.10 ± 0.27 | 58.45 ± 4.65 |
| | Soil 4 | 57.00 ± 0.80 | 4.13 ± 0.13 | 61.00 ± 1.60 |
| | Soil 5 | 47.95 ± 3.65 | 3.96 ± 0.20 | 54.90 ± 5.20 |
| HN-B | Dehusked rice grain S1 | 0.102 ± 0.002 | 0.236 ± 0.013 | 2.22 ± 0.021 |
| | Dehusked rice grain S2 | 0.101 ± 0.001 | 0.161 ± 0.010 | 1.86 ± 0.037 |
| | Dehusked rice grain S3 | 0.112 ± 0.001 | 0.051 ± 0.004 | 1.92 ± 0.064 |
| | Dehusked rice grain S4 | 0.126 ± 0.002 | 0.024 ± 0.001 | 1.41 ± 0.034 |
| | Dehusked rice grain S5 | 0.139 ± 0.003 | 0.028 ± 0.001 | 1.51 ± 0.122 |
| | Rice husk S1 | 0.227 ± 0.013 | 0.182 ± 0.005 | 2.49 ± 0.529 |
| | Rice husk S2 | 0.222 ± 0.006 | 0.124 ± 0.003 | 1.92 ± 0.034 |
| | Rice husk S3 | 0.213 ± 0.002 | 0.037 ± 0.000 | 1.90 ± 0.035 |
| | Rice husk S4 | 0.282 ± 0.011 | 0.026 ± 0.005 | 1.74 ± 0.101 |
| | Rice husk S5 | 0.331 ± 0.014 | 0.022 ± 0.002 | 1.73 ± 0.014 |
| | Soil 1 | 38.1 ± 4.10 | 2.77 ± 0.004 | 48.45 ± 2.35 |
| | Soil 2 | 40.80 ± 0.70 | 2.45 ± 0.09 | 52.25 ± 0.95 |
| | Soil 3 | 30.10 ± 1.30 | 2.12 ± 0.07 | 42.30 ± 0.60 |
| | Soil 4 | 35.20 ± 2.50 | 2.33 ± 0.12 | 49.65 ± 2.15 |
| | Soil 5 | 25.00 ± 1.60 | 1.83 ± 0.17 | 34.10 ± 0.20 |

Note: Data are expressed as means ± S.E.M for duplicate samples at each sampling point.

**Table 3.** Concentrations (mg/kg) of arsenic (As), cadmium (Cd) and copper (Cu) in the samples from Jiangxi province (JX).

| Sampling Sites | Sample Id | As (mg/kg) | Cd (mg/kg) | Cu (mg/kg) |
|---|---|---|---|---|
| JX-A | Dehusked rice grain S1 | 0.143 ± 0.005 | 0.102 ± 0.009 | 3.35 ± 0.152 |
| | Dehusked rice grain S2 | 0.140 ± 0.005 | 0.130 ± 0.001 | 3.73 ± 0.103 |
| | Dehusked rice grain S3 | 0.158 ± 0.011 | 0.069 ± 0.004 | 3.12 ± 0.065 |
| | Dehusked rice grain S4 | 0.155 ± 0.006 | 0.076 ± 0.001 | 3.23 ± 0.016 |
| | Rice husk S1 | 0.358 ± 0.044 | 0.055 ± 0.004 | 3.78 ± 0.796 |
| | Rice husk S2 | 0.266 ± 0.008 | 0.093 ± 0.004 | 3.03 ± 0.019 |
| | Rice husk S3 | 0.273 ± 0.025 | 0.068 ± 0.026 | 2.42 ± 0.278 |
| | Rice husk S4 | 0.360 ± 0.014 | 0.107 ± 0.013 | 3.38 ± 0.006 |
| | Soil 1 | 9.92 ± 0.29 | 0.25 ± 0.03 | 24.1 ± 2.3 |
| | Soil 2 | 9.35 ± 0.10 | 0.24 ± 0.02 | 23.1 ± 0.9 |
| | Soil 3 | 8.60 ± 0.68 | 0.20 ± 0.01 | 24.1 ± 0.8 |
| | Soil 4 | 8.01 ± 0.24 | 0.20 ± 0.01 | 22.3 ± 0.6 |
| | Soil 5 | 8.68 ± 0.17 | 0.23 ± 0.01 | 21.6 ± 0.7 |
| JX-B | Dehusked rice grain S1 | 0.180 ± 0.003 | 0.424 ± 0.026 | 4.12 ± 0.142 |
| | Dehusked rice grain S2 | 0.177 ± 0.002 | 0.421 ± 0.016 | 4.96 ± 0.195 |
| | Dehusked rice grain S3 | 0.155 ± 0.000 | 0.461 ± 0.000 | 4.57 ± 0.047 |
| | Dehusked rice grain S4 | 0.178 ± 0.002 | 0.425 ± 0.011 | 3.47 ± 0.038 |
| | Dehusked rice grain S5 | 0.203 ± 0.018 | 0.535 ± 0.000 | 4.69 ± 0.104 |
| | Rice husk S1 | 0.331 ± 0.023 | 0.138 ± 0.002 | 3.96 ± 0.081 |
| | Rice husk S2 | 0.304 ± 0.017 | 0.130 ± 0.006 | 4.68 ± 0.406 |
| | Rice husk S3 | 0.260 ± 0.018 | 0.153 ± 0.006 | 4.76 ± 0.191 |
| | Rice husk S4 | 0.309 ± 0.001 | 0.139 ± 0.015 | 3.64 ± 0.125 |
| | Rice husk S5 | 0.346 ± 0.030 | 0.214 ± 0.003 | 4.59 ± 0.407 |
| | Soil 1 | 4.48 ± 0.10 | 0.29 ± 0.01 | 19.2 ± 0.8 |
| | Soil 2 | 3.63 ± 0.04 | 0.28 ± 0.03 | 18.6 ± 1.8 |
| | Soil 3 | 3.82 ± 0.26 | 0.34 ± 0.02 | 21.3 ± 1.3 |
| | Soil 4 | 3.40 ± 0.10 | 0.30 ± 0.02 | 18.9 ± 0.2 |
| | Soil 5 | 4.31 ± 0.14 | 0.29 ± 0.01 | 19.5 ± 0.7 |

Note: Data are expressed as means ± S.E.M for duplicate samples at each sampling point.



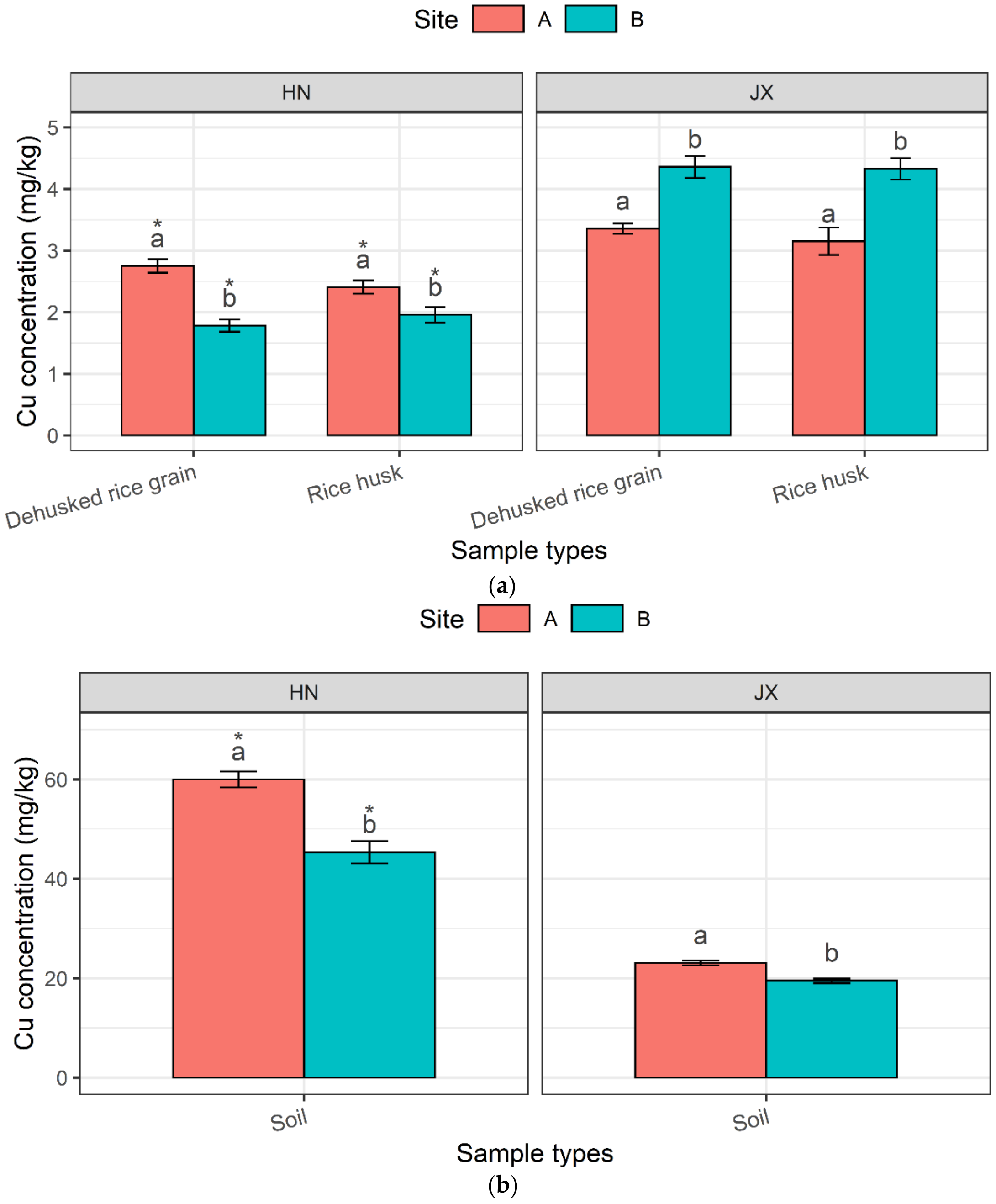
(**a**)

(**b**)

**Figure 4.** Cadmium (Cd) concentrations in the paired dehusked rice grain, rice husk (**a**) and soil samples (**b**) from two sampling sites in Hunan (HN) and Jiangxi (JX) provinces; lower-case letter indicates a significant difference ($p < 0.05$) between two sites in the same province, while the * symbol presents the differences ($p < 0.05$) at two sites across the two provinces.

In addition, ratios of Cd in dehusked grains to soil were much higher for Cd compared with As in this study, which indicates Cd is more readily taken up by rice and easier to be accumulated in the grain. This is in accordance with previous research [45], which also verified that different factors influence the bioavailability of As and Cd in soil and As and Cd transport into the grains [46]. Being nonessential to the plants, As and Cd enter the plants via the transporters of essential elements. For example, rice plants assimilate As (III) and As (V) through transporters of silica acid (OsNIP2;1) and phosphate (OsPHF1, OsPHF2), respectively, while taking up Cd via Fe(II) iron-regulated transporter 1 (IRT1) and manganese (Mn) transporters (OsNramp5) [44].

Cu is essential for plants and humans. Cu concentrations in the dehusked rice grains were higher than in the husk. Notably, Cu concentrations in rice were negatively correlated with those in the soil (Figure 5, Tables 2 and 3). Currently, there are no limits for Cu in crop-based food products. However, the concentrations of Cu in the soils were 59.97, 45.35, 23.04, and 19.48 mg/kg, respectively, from HN-A, HN-B, JX-A and JX-B, with 65.0% of soil samples from Hunan exceeding the national standard (50 mg/kg when pH < 6.5) for farming soil in China (GB15618-2018). While Cu is an important agrichemical, techniques are being developed to reduce its use in agriculture. For example, nanotechnology is one of the efficient methods to reduce the application dose of Cu used in farming.



(**a**)

(**b**)

**Figure 5.** Copper (Cu) concentrations in the paired dehusked rice grain, rice husk (**a**) and soil samples (**b**) from two sampling sites in Hunan (HN) and Jiangxi (JX) provinces; lower-case letter indicates a significant difference ($p < 0.05$) between two sites in the same province, while the * symbol presents the differences ($p < 0.05$) at two sites across the two provinces.

## 4. Conclusions

Although having been studied for several decades, HM pollution in agricultural soil is still a big concern due to continuing urbanization and rapid industrialization. This paper presented results from a field sampling study in four paddies located in Hunan and Jiangxi provinces. Concentrations of As, Cd and Cu in the soil and paired rice plants were obtained. The accumulations of As and Cd in rice grains pose potential risks to humans, especially to younger populations, since 73.7% and 89.5% of the dehusked rice grain samples exceeded the proposed limits of As and Cd, respectively, in rice products for children (As 100 µg/kg, Cd 40 µg/kg). In addition, rice husks, as an important byproduct of rice plants, accumulate higher concentrations of As, which should be considered when husks are used as food products or additives. The different distribution patterns of As and Cd indicate that the transport of As and Cd from soil to rice grains depends not only on their total content in the soil, but also the environmental factors, especially pH and OM, together with the transport mechanisms inside the plants. Although not regulated in rice products, Cu in the soil from the sampling sites is approaching the national standard (GB15618-2018), which should draw the attention to Cu-based agrichemical application during farming operations. With little industrial influence, the paddy soils were still heavily polluted by HMs. Novel methodology should be adopted to alleviate the pollution from the source by conventional farming process. Results from this study can contribute to the body of fundamental data regarding agricultural soil condition investigation and risks of rice products and byproducts to animals and humans.

**Author Contributions:** Conceptualization, J.L.; methodology, J.L.; software, J.L.; validation, J.S., J.W. and X.S.; formal analysis, J.L., J.S., J.W. and X.S.; investigation, J.S., J.W. and X.S.; resources, J.L., H.W.; data curation, J.L.; writing—original draft preparation, J.L., J.S. and J.W.; writing—review and editing, J.L. and H.W.; visualization, J.L.; supervision, J.L.; project administration, J.L.; funding acquisition, J.L. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was supported by the Environmental Research Institute Liu Jing Young Scholar Future Plan at Shandong University, China, and the Youth Fund of Natural Science Foundation from Shandong Province, China (ZR2021QD019).

**Acknowledgments:** The authors thank Gang Wu from Jiangxi and Haiyu Wang from Hunan for their help in collecting the samples. We thank Chengjia Zhang and Nannan Dong from Core Facilities for Life and Environmental Sciences (State Key Laboratory of Microbial Technology, Shandong University) for assistance in elemental analysis using ICP–MS (NexION 1000G). We also thank Naiseng Yang at Shandong University for mapping the sampling sites.

**Conflicts of Interest:** The authors declare no competing financial interest.

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