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Factors Affecting Dietary Intake of Copper and Zinc via Rice Consumption by Residents of Major Rice-Producing Regions in China

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Abstract: Background: Copper (Cu) and zinc (Zn) are essential nutrients that must be maintained at adequate levels in the human body in order to make physiological functions normal and sustainable. Rice is a leading staple cereal crop which can be the main source of Cu and Zn in the diet. Results: Here, we aimed to investigate Cu and Zn concentrations in rice with corresponding soil influencing factors and to assess the dietary intake of Cu and Zn from rice consumption by residents of major rice producing regions. A total of 712 rice grain and 90 paired soil–rice samples were collected from September to November 2015 covering eleven provinces across China. Average Cu and Zn concentrations were 27.2 and 69.1 mg kg^{-1}, respectively, in soils, and 1.98 and 12.3 mg kg^{-1} in rice. The concentrations and bioconcentration factors (BCFs) of Cu and Zn followed the sequence: roots > shoots > grains. Soil pH, cation exchange capacity (CEC), and soil organic carbon (SOC) play important roles in rice Cu and Zn uptake with negative effects. The average Cu and Zn intakes from rice consumption were 0.597 and 3.68 mg day^{-1}, respectively. Conclusions: The status of Cu and Zn daily intake from rice consumption were fully adequate but there remained some sampling sites where Zn intake for males and Cu intakes were deficient at 1.40%, indicating that local residents need to maintain their dietary nutrient requirements.

Keywords: China; zinc; copper; daily intake; rice; soil

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1. Introduction

Copper (Cu) and zinc (Zn) are essential micronutrients that must be kept at adequate levels in the human body to maintain normal physiological functions, with a requirement of only several milligrams per day [1–3]. Zinc is necessary for the normal growth and sustainability of the human body and has been shown to modulate erythropoiesis, immunity to infectious diseases, and iron metabolism, which play important role in sustainable development of the world population [4]. Cu is also an essential trace element, with approximately 100 mg in the human body [3]. Lam et al. found an inverse association between serum Cu concentrations and cognitive performance in a large cohort of elderly healthy women [5]. A high intake of Cu is associated with a good metabolic profile. However, Cu and Zn may be harmful at excessive levels of exposure but may give rise to malnutrition when their ingestion rates are too low [3,6]. Deficiency and excess of Cu and Zn intake are both harmful to human health.

Over two-thirds of the global population lack one or more essential micronutrients in their diet [7]. It is estimated that over 30% of people worldwide facing Zn and Cu deficiencies and suboptimal zinc status have been recognized in many groups of the population in both less developed and industrialized countries [4,8,9]. Dietary Cu and Zn deficiency may lead to adverse consequences throughout the human life span. Prolonged marginal Cu deficiency has been associated with alterations in cholesterol metabolism in adulthood [1]. Numerous studies have reported that Zn deficiency can result in slow physical growth, poor appetite, and diminished taste acuity among healthy infants and children [2,4]. In contrast, excessive intake can lead to toxic effects [10]. Cu and Zn can be released into the environment due to industrial agricultural activities. High Cu and Zn concentrations have been observed in the Guangdong and Yangtze River Delta area [11–14].

Rice (*Oryza sativa* L.) is a leading staple cereal crop feeding more than 50% of the global population and the quality of rice plays an important role in human health [15,16]. The diet can provide many essential micronutrients and rice is the dominant food in the human diet in China. Rice can, therefore, guarantee the sustainability of micronutrients in regions where it is the main staple food. Cu and Zn are the most abundant metals in rice because they are micronutrients that were essential to the growth of rice [17]. Thus, gradual accumulation of Cu and Zn in rice grains and their subsequent transfer to the human food chain is a major source of Cu and Zn [15]. It is very important to ascertain the Cu and Zn concentrations in rice and to further investigate whether or not Cu and Zn intakes via rice are adequate, which can reveal the sustainability of Cu and Zn consumption via rice.

Cu and Zn concentrations in rice are, therefore, of increasing concern due to food safety issues and potential risks to human health. Knowledge of Cu and Zn concentrations in rice and assessment of their intake are important in monitoring possibly deficiencies or toxicities. Cu and Zn deficiencies are commonly caused by inadequate dietary intake, increased losses from the body, and increased physiological requirements. In addition, the inadequate dietary intake of micronutrients has been attributed to low intake of foods rich in these elements and to their low bioavailability in food products [7]. In general, plant accumulation of mineral elements depends on their availability in the rhizosphere soil solution, unless foliar fertilizers are applied [7]. The availability of elements can be influenced by soil properties such as soil pH, CEC (soil cation exchange capacity), SOC (soil organic matter content), and clay content [12,13,18–20]. Thus, although high Cu and Zn concentrations may occur in soils, the Cu and Zn in food crops may not high, indicating that soil properties have affected plant uptake of Cu and Zn. It is, therefore, necessary to investigate the influence of soil properties on Cu and Zn intakes from rice.

Here, we determined Cu and Zn concentrations in the soil–rice system in major rice producing regions of China and examined the influence of soil properties on plant Cu and Zn uptake. In addition, the daily intakes of Cu and Zn from rice consumption were also calculated by referring to data in the Fourth China Total Diet Study to assess whether the human Cu and Zn intakes are sufficient. This study will provide new information on health risks from Cu and Zn intakes via rice consumption by residents who eat rice as their main food.

2. Materials and Methods

2.1. Rice and Soil Collection

A total of 802 rice grains were collected in the major rice producing areas from September to November 2015 covering eleven provinces throughout China. The rice grain sampling sites were distributed in the provinces of Heilongjiang (HLJ, n = 24), Anhui (AH, n = 18), Zhejiang (ZJ, n = 142), Jiangsu (JS, n = 130), Yunnan (YN, n = 21), Hunan (HN, n = 200), Guangdong (GD, n = 27), Fujian (FJ, n = 22), Guizhou (GZ, n = 42), Jiangxi (JX, n = 116), and in the autonomous region of Guangxi (GX, n = 60). In addition, a total of 90 paired soil and rice plant samples located in the sites of the selected 90 rice grain samples were collected to examine the main soil properties which may influence Cu and Zn uptake from soil by rice. Rice samples were collected in triplicate when mature at the paired rice and soil sites. After collecting, the rice samples were separated into roots, sterns, and grains. The soils in corresponding rice plants were also collected at the depth of top 20 cm. All the geographical locations of grain sampling sites are shown in Figure 1. About 0.5 kg rice grains were collected randomly in the sampling areas at maturity.

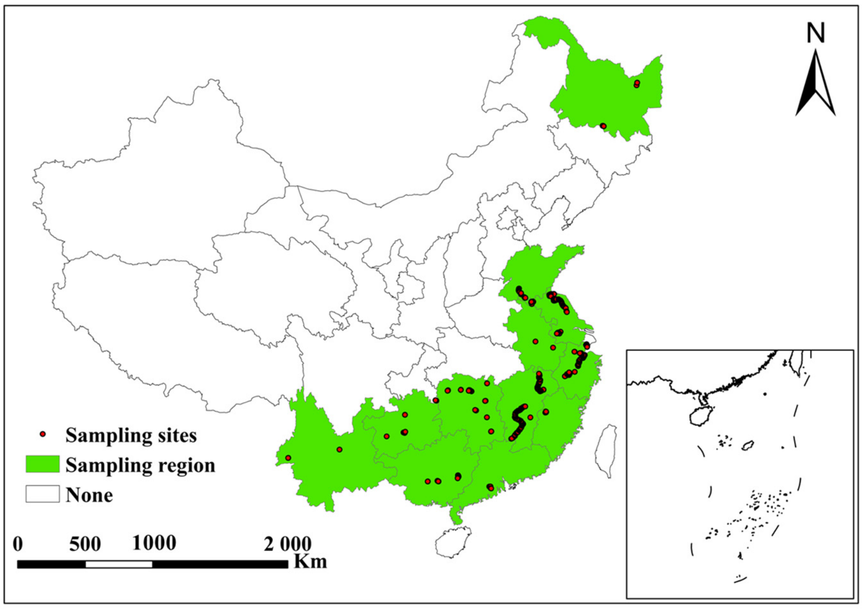


Figure 1. Geographical locations of sampling sites in the major rice producing regions.

2.2. Sample Preparation and Chemical Analysis

Plants were separated into roots, shoots, and grains, taken to the laboratory, washed with tap water three times, and then with distilled water three times and dried in oven at 70 °C until constant weight. The husks were peeled from trice grains and the brown rice was further polished with a polishing machine. The root, shoot, and polished rice samples were ground using a stainless-steel mill and stored prior to chemical analysis. The soil samples collected were air-dried and ground to pass 2-mm and 0.15-mm nylon sieves for further chemical analysis. Soil pH was measured at a 1:2.5 (w/v) soil:water ratio. SOC was determined by the potassium dichromate wet combustion method. CEC was measured by exchange with ammonium acetate (1.0 mol L^{-1}, pH 7.0) and titration with HCl. Soil clay content was measured by the pipette method which described in Lu (2000) [21]. Plant samples were digested with a mixture of 2 mL HNO_3 and 4 mL H_2O_2 and the soil samples were with a mixture of 5 mL HCl and 5 mL HNO_3 in sealed digestion containers. Cu and Zn concentrations in the digests were determined by atomic absorption spectrophotometry (AAS, SpectrAA 220FS and SpectrAA 240Z, Varian, Palo Alto, CA, USA). Quality control was conducted using reagent blanks in each bath of samples. Certified reference materials GBW € 100,348 (rice) and GSS-5 (soil) were obtained from the Chinese National Research Centre for Standards, Langfang, Hebei and were used in each digestion batch. The concentrations of Cu and Zn determined in the standard reference materials were in good agreement with their certified values (100 ± 10).

2.3. Assessment of Cu and Zn Intakes via Rice Consumption

The theoretical Cu and Zn concentrations ($C_{calculated}$) that can ensure the recommended reference intakes of Cu and Zn were calculated to compare with the measured Cu and Zn concentrations in rice grains. $C_{calculated}$ was calculated using the following equation.

$$C_{calculated} = \mathrm{RNI} \times R_{\mathrm{cereal}} \times R_{\mathrm{rice}}/\mathrm{DC} \tag{1}$$

where $C_{calculated}$ is the calculated Cu or Zn concentration in mg kg^{-1} based on the recommended intake value in the Chinese Nutrition Society [22]; RNI is the recommended reference intake of the standard population in the Chinese Dietary Reference Intakes in mg day^{-1} (Cu, 2 mg day^{-1}; Zn for males, 15 mg day^{-1} and for females, 11.5 mg day^{-1}) [22]; R_{cereal} is the estimated cereal source of dietary Cu or Zn intake in % according to the Fourth China Total Diet Study (Table S1) and the cereal sources of dietary Cu and Zn intake are 51.1% and 42.2%, respectively [23]; R_{rice} represents the ratio of the amount with rice consumption to cereal consumption in %; and DC is the amount of daily consumption of rice of the standard population in g day^{-1}.

Then, the calculated Cu and Zn concentrations and the actual Cu and Zn concentrations in rice were calculated as follows.

$$Q = C_{calculated}/C_{measured} \tag{2}$$

where $C_{measured}$ is the actual concentration of Cu or Zn in rice grains in mg kg^{-1}. A value of $Q \leq 1$ indicates a deficiency of Cu or Zn intake from rice consumption. In contrast, a value of $Q > 1$ indicates an adequate intake from rice consumption and the possibility of health risk due to excessive Cu or Zn.

2.4. Assessment of Soil Pollution and Enrichment with Cu and Zn

The single pollution index (PI) value of Cu or Zn in soil was calculated as follows.

$$PI = C_{measured}/C_{Standard} \tag{3}$$

where $C_{measured}$ is the measured total Cu or Zn concentration and $C_{Standard}$ was the maximum level of Cu (50 mg kg^{-1} for $pH \leq 6.5$, 100 mg kg^{-1} for $pH > 6.5$) or Zn (200 mg kg^{-1} for $pH \leq 6.5$, 250 mg kg^{-1} for $6.5 < pH \leq 7.5$ and 300 mg kg^{-1} for $6.5 < pH \leq 7.5$ mg kg^{-1} for $pH > 7.5$) in soils according to the Soil Environmental Quality standard (GB 15618-2018) [24].

The bio-concentration factors (BCFs) of Cu and Zn in rice roots, shoots, and grain were calculated as follows.

$$BCF = C_{root} \text{ or } C_{shoot} \text{ or } C_{grain}/C_{soil} \tag{4}$$

The BCF is the ratio between the Cu or Zn concentration in rice roots, shoots, and grain and the total concentration in soil (both in mg kg^{-1}).

2.5. Statistical Analysis

All data in this study were analyzed using Microsoft Excel (2019) and the SPSS 20.0 for Windows statistical package. In order to test the differences in Cu and Zn concentrations and BCF among the 11 sampling sites ($p < 0.05$), one-way analysis of variance (ANOVA) with the least significant difference test was used in data analysis. If the residuals from ANOVA were not normally distributed or heteroscedasticity was detected by Levene's test, the data were all $\log_{10}$-transformed, but the mean and standard deviation (SD) values presented here are those of the non-transformed data. Pearson correlation analysis was used to study the influence of soil properties to Cu and Zn concentrations in rice roots, shoots, and grain. The contributions of soil properties to Cu and Zn accumulation in rice grains were calculated with the use of Generalized Boosted Models (GBM) using the gbm package within the R 3.2.2 statistical platform. Details of GBM analysis are presented in the study of Mu et al. [25]. Soil total Cu and Zn concentrations, pH, SOC, CEC, and clay contents were used as prediction factors to calculate the contribution of different soil parameters to the Cu and Zn concentrations in rice roots, sterns, and grain.

3. Results

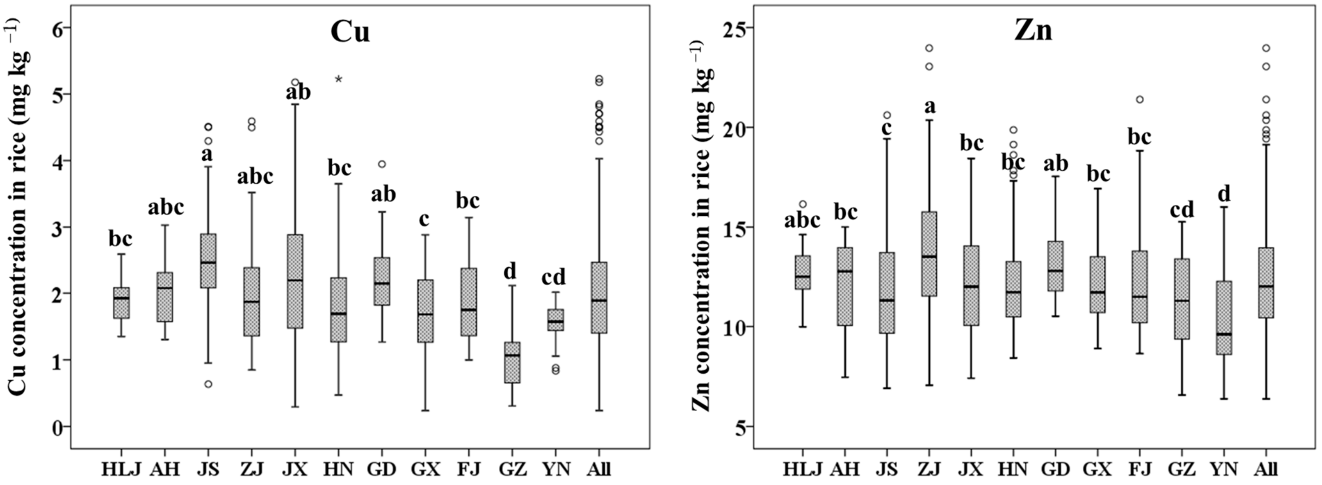
3.1. Transfer of Cu and Zn in the Soil–Plant System at Different Sampling Sites

The average values of pH, SOC, CEC, and clay percentage of the soils collected were 5.92, 20.4 g kg^{-1}, 11.6 cmol (+) kg^{-1}, and 22.9%, respectively (Table 1). Soil pH ranged from strongly acid to weakly calcareous. Soil Cu and Zn concentrations ranged from 3.23 to 179 and from 17.6 to 124 mg kg^{-1} with mean values of 27.2 and 69.1 mg kg^{-1}, respectively. Three soil samples (3.33% of 90) may represent potential Cu contamination risk according to the safety of agricultural produce on account of the risk screening values (50 mg kg^{-1} for $pH \leq 6.5$, 100 mg kg^{-1} for $pH > 6.5$) for soil contamination of agricultural land according to the Chinese Soil Environmental Quality standard (GB 15618-2018) [24]. The average Cu and Zn concentrations in roots and shoots were 20.7 and 52.2 and 4.10 and 45.5 mg kg^{-1}, respectively (Table 1). In addition, as shown in Figure 2, Cu and Zn concentrations in the 802 rice samples were 1.98 (0.236–5.23) and 12.3 (2.62–23.9) mg kg^{-1}. The highest Cu and Zn concentrations in rice were 2.49 (Jiangsu) and 13.7 (Zhejiang) mg kg^{-1}, respectively, and the lowest Cu and Zn concentrations in rice were 1.04 (Guizhou) and 10.5 (Yunnan) mg kg^{-1}, respectively. Cu and Zn bio-concentration factors (BCF) in roots, shoots, and grain were 1.06, 0.219, and 0.103, and 0.978, 0.853, and 0.225, respectively. The maximum and minimum Cu and Zn BCFs of roots, shoots, and grains all occurred at Guangdong and Guizhou (Figure 3). The sequence of the Cu and Zn BCF values was $BCF_{root} > BCF_{shoot} > BCF_{grain}$.

Table 1. Soil properties and Cu and Zn concentrations in the 90 paired samples.

Statistic	pH	CEC [a] (cmol (+) kg^{-1})	SOC [b] (g kg^{-1})	Clay (%)	Soil [c]		Roots [c]		Shoots [c]	
					Cu	Zn	Cu	Zn	Cu	Zn
Minimum	4.16	2.66	6.48	6.64	3.23	17.6	4.49	15.4	1.00	7.19
Maximum	7.97	27.1	60.5	49.9	179	124	82.7	158	16.5	120
Mean	5.92	11.6	30.4	22.9	27.2	69.1	20.7	52.2	4.10	45.5
SD	0.89	5.49	10.6	8.54	25.4	24.5	16.7	31.0	2.53	25.2

[a]: Cation exchange capacity (buffered); [b]: Soil organic carbon; [c]: the units of Cu and Zn concentration in soil, roots, and shoots are mg kg^{-1}.



Note: Letters of the Cu and Zn concentration in different provinces represent significant differences ($p < 0.05$) by one-way analysis of variance among t areas.

Figure 2. Cu and Zn concentrations in polished rice.

3.2. Factors Influencing Cu and Zn Transfer in the Soil–Plant System at Different Sampling Sites

Pearson correlation analysis (Table 2) shows that soil pH was significantly and negatively correlated with the concentrations of Cu in shoots and rice grains ($p < 0.01$). There was no significant correlation between Cu in roots and soil pH, indicating that the enrichment of Cu in the roots was not mainly influenced by soil pH, but the bioavailability of Cu to shoots and grains was low in soils with high pH. In addition, SOC was also significantly and negatively correlated with the concentrations of Cu in roots, shoots, and grain ($p < 0.01$) indicating that high SOC may reduce the uptake of Cu by the plants. In comparison, the Zn concentrations in roots, shoots, and grain were all significantly and negatively correlated with soil pH ($p < 0.01$) and the correlation coefficients were higher than those of Cu, indicating that the plant accumulation of Zn was more sensitive than that of Cu to changes in soil pH. Soil CEC was also significantly and negatively correlated with the Zn concentrations in roots ($p < 0.01$), shoots ($p < 0.01$), and grain ($p < 0.05$). There was no significant correlation between total Cu and Zn in grains and in soils indicating that the accumulation of Cu and Zn in grains was not influenced by soil total Cu and Zn, but soil properties may influence the solubility of soil Cu and Zn. In addition, the contribution of soil properties to Cu and Zn concentrations in roots, shoots, and grain were calculated with GBM analysis. Soil variables (except pH) were $\log_{10}$-transformed to ensure homogeneity of variance. As shown in Figure 4, the sequence of the contribution rates for Cu accumulation in grain, shoots, and roots was SOC (21.9%) > pH (18.8%) > CEC (16.2%) > clay (15.9%) > Cu (13.9%) > Zn (13.3%), pH (18.9%) > SOC (18.8%) > CEC (16.4%) > Cu (16.1%) > clay (15.4%) > Zn (14.4%), and SOC (19.5%) > pH (18.1%) > CEC (17.3%) > Cu (15.5%) > clay (15.4%) > Zn (14.2%), respectively. The corresponding values for Zn were pH (19.6%) > CEC (17.5%) > Zn (17.1%) > SOC (16.7%) > clay (16.4%) > Cu (12.7%), pH (32.4%) > CEC (14.9%) > Zn (14.7%) > SOC (14.2%) > clay (12.3%) > Cu (11.5%), and CEC (22.9%) > pH (21.1%) > SOC (17.2%) > Cu (1.7%) > clay (13.5%) > Zn (11.6%), respectively. The contribution rates of soil properties differed significantly between Cu and Zn concentrations in roots, shoots, and grain indicating that the effects of soil properties on Cu and Zn accumulation would be different in different parts of the plants.

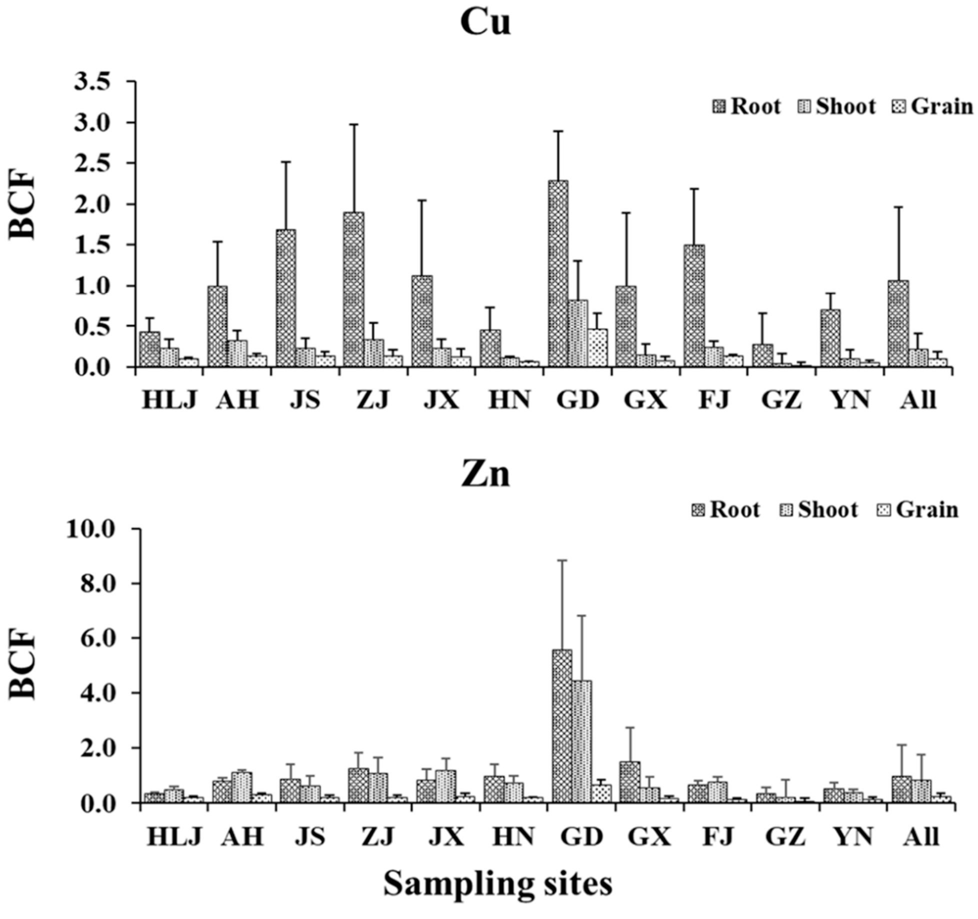


Figure 3. Cu and Zn BCFs of roots, shoots, and rice at sampling sites in different provinces.

3.3. Daily Intake of Cu and Zn from Rice Consumption at Different Sampling Sites

The Cu and Zn intakes from rice consumption were calculated with measured Cu and Zn concentrations and the amount of rice consumed using data from a survey made by the Chinese National Nutrition and Health Survey (CNNHS) in 2002 (Table S1). This report also gave the total daily intake of Cu and Zn from total food consumption. The average Cu and Zn intakes from rice consumption were 0.597 and 3.68 mg day^{-1}, respectively. The ratios of Cu and Zn intake from rice consumption to total intake are shown in Figure 5. The average percentages of Cu and Zn intake from rice consumption to total intake were 27.7% and

31.2%, respectively. The maximum and minimum ratios of Cu intake from rice consumption were 42.1% (Anhui) and 17.2% (Guizhou) because the highest rice consumption occurred in Anhui and the lowest Cu concentration in rice occurred in Guizhou. The maximum and minimum ratios of Zn intake from rice consumption were 42.3% (Guangdong) and 24.5% (Jiangsu). The structure of dietary and intake of Cu and Zn differed among the main rice consumption provinces.

Table 2. Pearson correlation analysis of the 90 soil properties and Cu and Zn concentrations in different parts of rice plants.

Metal		pH	CEC	SOC	Clay	Soil	Roots	Shoots	Rice
Cu	pH	1							
	CEC	0.542 **	1						
	SOC	0.232 *	0.447 **	1					
	Clay	0.041	0.298 **	0.185	1				
	Soil	0.236 *	0.291 **	0.465 **	0.369 **	1			
	Root	−0.118	−0.159	−0.335 **	0.049	0.077	1		
	Shoot	−0.393 **	−0.174	−0.349 **	0.104	0.008	0.667 **	1	
	Grain	−0.295 **	−0.267 *	−0.554 **	−0.021	−0.136	0.594 **	0.719 **	1
Zn	pH	1							
	CEC	0.542 **	1						
	SOC	0.232 *	0.447 **	1					
	Clay	0.041	0.298 **	0.185	1				
	Soil	0.269 *	0.242 *	0.472 **	0.188	1			
	Root	−0.416 **	−0.416 **	−0.159	−0.133	−0.099	1		
	Shoot	−0.723 **	−0.546 **	−0.404 **	−0.065	−0.368 **	0.592 **	1	
	Grain	−0.404 **	−0.257 *	−0.193	−0.065	−0.201	0.328 **	0.533 **	1

**: $p < 0.01$; *: $p < 0.05$.

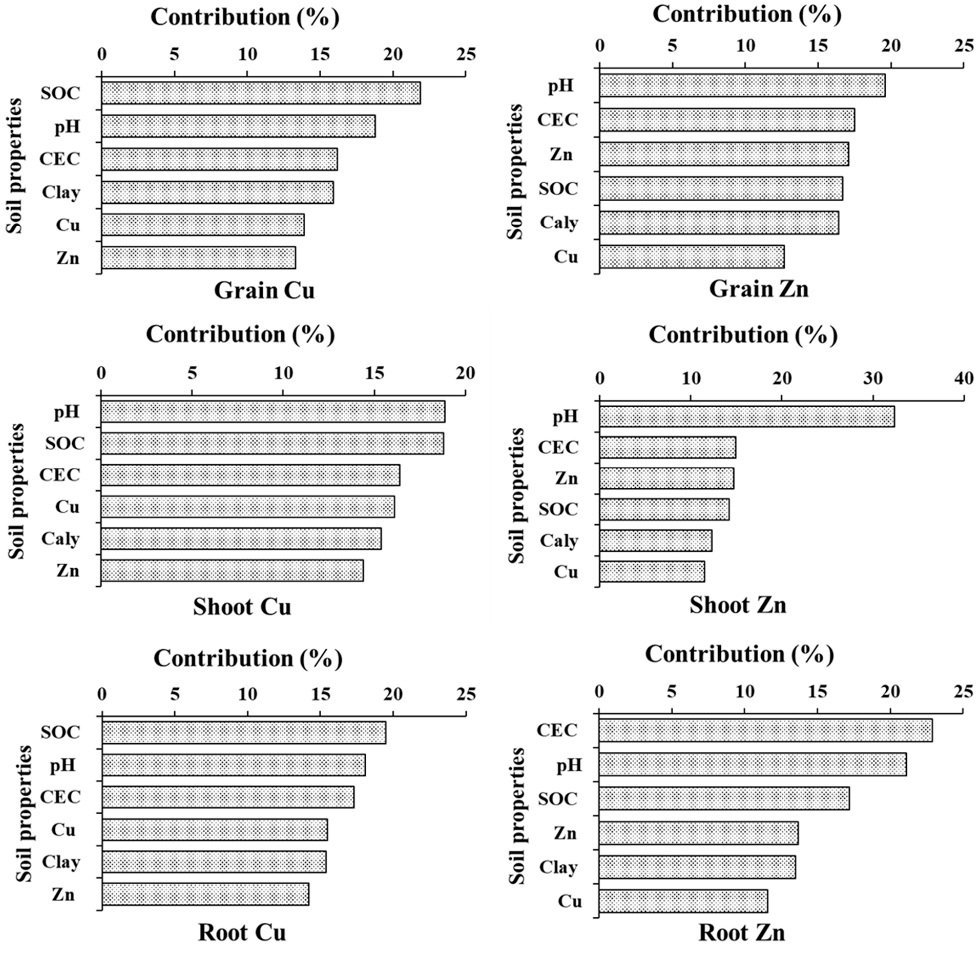


Figure 4. Contributions of soil properties to Cu and Zn concentrations in grains, shoots, and roots.

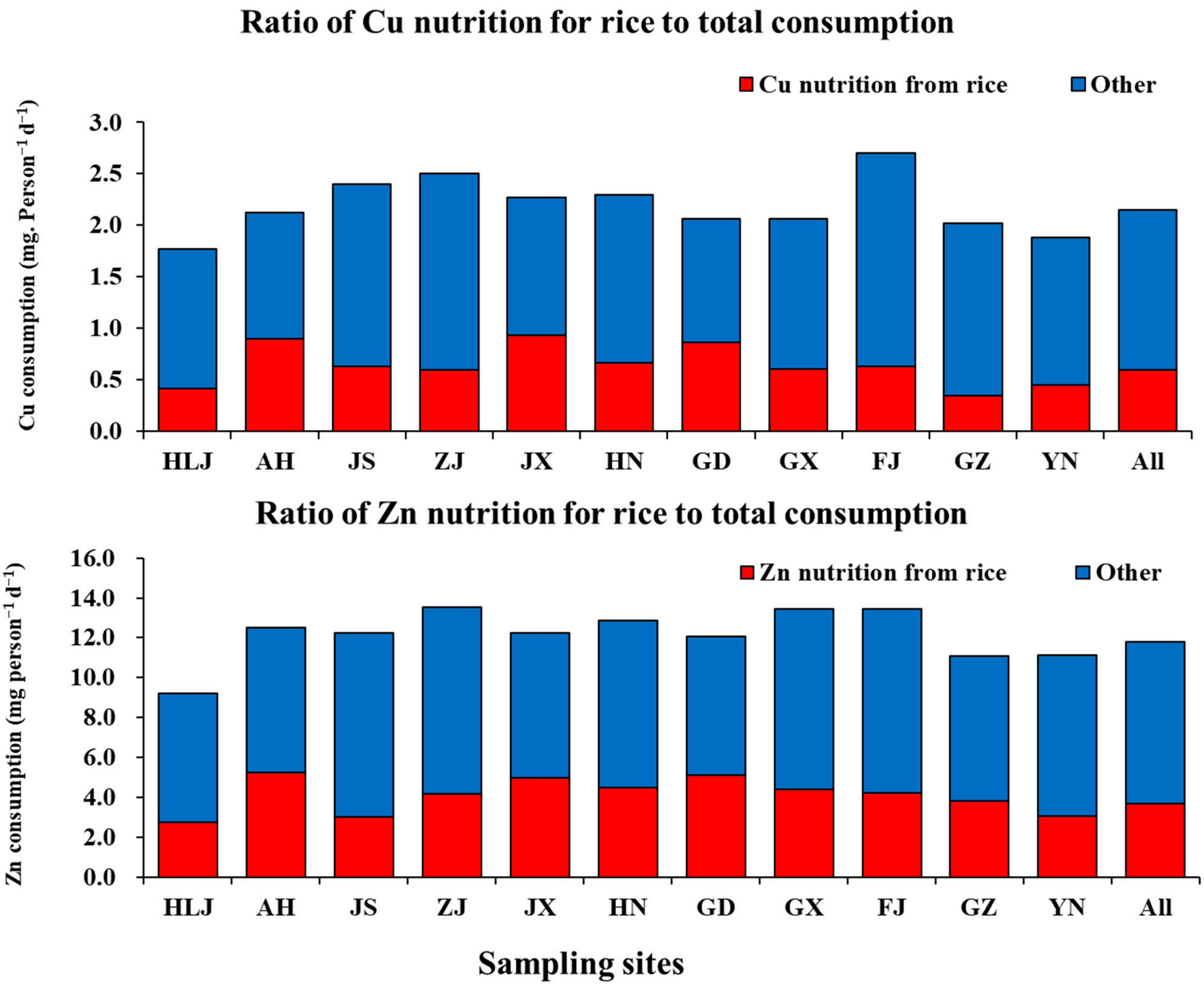


Figure 5. Ratios of the calculated Cu and Zn intake from rice consumption and total Cu and Zn intakes.

The adequacy of daily intakes of Cu and Zn from rice consumption at different sampling sites was investigated by calculating the theoretical Cu and Zn concentrations. And the values were calculated using the values of the recommended reference intakes of Cu and Zn of the standard population in the Chinese Dietary Reference Intakes, the ratios of intakes of Cu and Zn from cereal to total daily intake, and the ratio of rice consumption to cereal consumption. Comparison was then made between the calculated and measured Cu and Zn concentrations to verify the adequacy of the daily intake of Cu and Zn. As shown in Table S2, the Q values of Cu throughout all sampling sites exceeded 1, indicating that the total daily intakes of Cu were adequate. The minimum Q value was 0.414 in Guizhou, indicating that the Cu intake there was deficient, consistent with the results showing the minimum grain Cu concentration at Guizhou. The Zn Q values for females and males were different. The Q values of Zn for males at all sampling sites was 0.986, indicating that the total intake of Zn from rice consumption was slightly below adequate. There was no sampling site where the Q value for male exceeded 1, indicating that the intake of Zn for the male population from rice consumption in the sampling sites tended to be deficient. However, at seven sampling sites the Q values for female exceeded 1 indicating that the Zn intake for females was adequate. The minimum Zn Q value for females was 0.651 at Heilongjiang which had the minimum rice consumption rate.

4. Discussion

4.1. Cu and Zn Transfer in the Soil–Plant System

A field investigation on the Cu and Zn concentrations, their accumulation, and distribution in soils and rice was conducted in Jiangsu province. The results show that the mean values of Cu and Zn concentrations in soil and rice were 30.5 and 90.1, and 3.84 and 19.1 mg kg^{-1}, respectively [22]. The concentrations of Cu and Zn in soil and rice grain from Jiangsu in the present study were 20.5 and 62.5, and 2.49 and 11.9 mg kg^{-1}, respectively, somewhat lower than those of Hang et al. as industrial operations have started since the 1980s in the sampling area and have threatened the safety of agricultural production [22]. Cao et al. have also investigated 23 soil and rice samples irrigated with trace metal-polluted water in Jiangsu, and the Cu and Zn concentrations in soil and rice were 31.8 and 103, and 2.64 and 12.0 mg kg^{-1}, respectively [26]. Although the soil Cu and Zn in the study of Cao et al. were higher than in the present study, the concentrations of Cu and Zn in rice were roughly similar [26]. Zhou et al. collected 26 pairs of complete rice samples and corresponding soil samples from a typical industrial county of Jiangsu province, and the results show that soil Zn had accumulated moderately with a mean value of 69.1 mg kg^{-1} in soil and 39.8 mg kg^{-1} in rice grains [11]. Zhao et al. made an investigation which involved 96 soil and rice samples in Zhejiang province and found that most of the study areas were contaminated with Cu and Zn to different degrees [16]. A study, in which a total of 41 rice samples were collected throughout Guangdong province in 2015, found that the maximum concentration of Cu and Zn were below the threshold values regulated by the Chinese Food China Food Standard Agency, indicating that there was no apparent Cu and Zn pollution [27]. These results are consistent with the concentrations of Cu and Zn in rice in Guangdong in the present study.

Some further investigations of Cu and Zn in the soil–rice system have also been published. Chen et al. investigated 72 pairs of soil and rice samples in the Yangtze River Delta region and the average Cu and Zn concentrations in soil and rice were 38.7 and 105, and 3.55 and 16.4 mg kg^{-1}, respectively [12]. The average concentrations of Cu and Zn in this study were 27.2 and 69.1 mg kg^{-1}, respectively, in soil and 1.98 and 12.3 mg kg^{-1}, respectively, in rice, and three soil samples showed a Cu pollution risk. Li et al. investigated the health risks of metals to local residents via the consumption of food crops cultivated in reclaimed soils of the Pearl River Estuary and the results indicate that rice crops cultivated on the reclaimed farmland were highly contaminated with metals including Cu and Zn [13].

The average BCFs in rice in the present study were 0.111 (Cu) and 0.220 (Zn), lower values than 0.196 (Cu) and 0.258 (Zn) reported by Hang et al. [28]. The BCF of Cu in rice roots, shoots, and grain was lower than that of Zn, indicating a stronger accumulation of Zn than of Cu which and this is consistent with the results of Chen et al., Hang et al., and Wang et al. [12,28,29]. The sequence of the BCF values for Cu and Zn is $BCF_{root} > BCF_{stem} > BCF_{grain}$ indicating that the roots have the strongest ability to accumulate the metals. The concentrations of metals often vary widely in different plant parts and metal concentrations are significantly higher in the roots than in the shoots or grains [12,19]. Potentially toxic metals in roots generally originate from uptake by the roots of available fractions of metals in the soil pore water and they can be stored in non-edible organs, such as roots, which can act as a source of metals in the grains under certain conditions [11,12]. The average Cu and Zn concentrations in roots ranged from 11.8 to 47.4, and 22.7 to 131 mg kg^{-1}, respectively, and the corresponding ranges in the present study were 0.079–4.06 and 0.195–9.01 mg kg^{-1}, respectively [12].

4.2. Major Soil Factors Influencing Cu and Zn Transfer from Soil to Plant

There was no significant correlation between total plant Cu or Zn concentrations and soil concentrations, supporting the conclusions of Hu et al. and Zhang et al. [18,20]. This indicates that soil total Cu and Zn concentrations have little effect on plant Cu and Zn accumulation. Numerous studies indicate that soil physicochemical properties (soil pH, CEC, SOC, and clay content) can influence the availability of metals in paddy fields and may affect metal uptake by rice [12,13,16,18–20,30]. In general, soil pH had significantly negative relationships with Cu and Zn concentrations in rice (Table 2), indicating that as soil pH decreased, the accumulation of Cu and Zn by rice was enhanced as found in previous studies [12,13,30]. More H^+ can be released into the soil solution in low soil pH conditions and it can markedly enhance the dissolution and transfer of Cu and Zn from soil to roots, thereby increasing phyto-availability [12,13]. In contrast, high soil pH can reduce available Cu and Zn in the soil solution and consequently reduce the accumulation of Cu and Zn by the plants [30]. There was also a significantly negative correlation ($p < 0.01$) between shoot Cu and Zn concentrations and SOC which was opposite to the results of Zeng et al. [30]. There was no significant correlation between SOC and grain Zn concentration but a significant and negative correlation ($p < 0.01$) between these was observed by Zeng et al. [26]. The grain Cu concentration was significantly correlated with SOC ($p < 0.01$) (Table 1) in the present study, but high SOC tended to increase the accumulation and availability of Cu in rice grains in the studies of Zhou et al. and Li et al. [11,31]. The accumulation of Zn in grain was weakly correlated with SOC, suggesting that the transfer of Zn from soils to grains may have been influenced by other soil properties in the present study. The different effects of SOC on Cu and Zn accumulation by rice may be due to differences in SOC content and in the concentrations of metals in rice as influenced by specific ranges of soil properties [11]. Significant and negative correlations were observed between soil CEC and the Zn concentrations in roots ($p < 0.01$), shoots ($p < 0.01$), and grains ($p < 0.05$) and Cu concentrations in grains ($p < 0.05$) since high CEC may reduce the solubility of soil Cu and Zn and further decrease the accumulation of Cu and Zn by rice rains. No significant correlation was observed between clay content and Cu or Zn concentrations in rice. However, high clay content has been found to decrease the accumulation of Cu and Zn in grain and their availability in some previous studies [11,16,31].

4.3. The Cu and Zn Intake from Rice Consumption

The average Cu and Zn intakes from rice consumption were 0.597 and 3.68 mg day^{-1}, respectively. The estimated Cu and Zn intakes from the total diet were 2.05 and 15.3 mg day^{-1}, respectively. The Chinese Nutrition Society [22] provides recommended reference intakes of Cu of 2 and Zn for males of 15 and for females of 11.5 mg day^{-1}, respectively. The intakes of Cu and Zn from rice consumption were, therefore, appropriate in general. The estimated total intakes of Cu and Zn in popular foodstuffs in China are 6.25 and 37.5 mg day^{-1}, respectively [32], significantly higher than in the present study. A study which used a Total Diet Study to assess the dietary intakes of essential elements by local residents of Shenzhen city found that the total intakes of Cu and Zn were 1.11 and 7.47 mg day^{-1}, respectively, lower than the values in the major rice producing regions in the present study [10]. The estimated daily intakes of Cu and Zn via foods by adults near a lead/zinc mine spill in Hunan province were 7.95 and 69.5 mg day^{-1}, respectively, approximately four times those in the present study and the foods were polluted with potentially toxic metals [33]. In addition, the dietary pattens in other countries are significant different from those in China. The Cu and Zn intakes via foodstuffs were calculated at 1.14 and 12.0 mg day^{-1}, respectively, in Pavia, northern Italy, and 1.12 and 4.8 mg day^{-1}, respectively, in Rio de Janeiro, Brazil [3,6]. The dietary exposure estimates of Cu and Zn of the French population (from the 1st French Total Diet Study) were 0.98 and 8.66 mg day^{-1}, respectively, for adults [34], also lower than in China. Differences in dietary pattens also lead to different Cu and Zn intakes in different regions within countries, and people in areas subject to Cu and Zn deficiencies need to consume more food with higher Cu and Zn concentrations. Consumption of cereals and cereal products contributes 13.3 and 13.5% to the total Cu and Zn intake of local residents of Shenzhen [15]. However, Cu and Zn intakes from rice consumption only as a percentage of total daily intake were 27.7 and 31.2%, respectively, in the present study with higher intakes than that in Shenzhen. This may be due to a higher rate of consumption of rice in the major rice production areas investigated in the present study.

5. Conclusions

Here, the structure of the rice diet and the intakes of Cu and Zn via rice consumption were different throughout the main rice consumption regions in Chian. The levels of Cu and Zn in the soil–rice system were not particularly high or low, and the Cu and Zn daily intakes from rice consumption were fully adequate which can maintain the sustainability of human body. However, there were some sampling sites in Heilongjiang and Guangzhou provinces with potential Cu and Zn deficiencies for the male population, indicating that the local residents should consume more food with higher Cu and Zn concentration to meet their nutritional requirements. In addition, soil properties are important factors influencing rice Cu and Zn uptake. The sequence of the contribution rates for Cu and Zn accumulation in rice grains were SOC (21.9%) > pH (18.8%) > CEC (16.2%) > clay (15.9%) > Cu (13.9%) > Zn (13.3%), and pH (19.6%) > CEC (17.5%) > Zn (17.1%) > SOC (16.7%) > clay (16.4%) > Cu (12.7%), respectively. The contribution rates of soil properties were also different in Cu and Zn concentration in roots, shoots, and grains, indicating that the effects of soil physicochemical properties on Cu and Zn accumulation are different in different plant parts.

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