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Research Article

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Variations in cadmium, mercury and copper accumulation among different rice cultivars in the Yangtse River Delta, China

[1]Junyu He*, [1]Yanfang Ren, [2]Cheng Zhu and [3]Dean Jiang

[1]*College of Agriculture, Guizhou University, Guiyang, China*
[2]*College of Life Science, China Jiliang University, Hangzhou, China*
[3]*College of Life Science, Zhejiang University, Hangzhou, China*

ABSTRACT

Heavy metals in polluted soils can accumulate in plants and threaten crop safety. A field experiments were conducted to investigate cadmium, mercury and copper accumulation in rice grains of 38 cultivars commonly cultivated in the Yangtse River Delta, to evaluate the contributions to the daily intake of the heavy metals from rice and to screen for low accumulative cultivars. The results showed the concentrations of cadmium, mercury and copper were 1.72-714.31 μg kg^{-1}, 1.12-58.98 μg kg^{-1} and 1.81-1.29 mg kg^{-1}, respectively. There was significantly positive relationship between cadmium and mercury, negative relationships between mercury and copper. Some rice grains contained high levels of heavy metals beyond the permissible levels given by FAO and WHO for human consumption. When the mean levels of cadmium, mercury and copper (170.93 μg kg^{-1}, 20.05 μg kg^{-1} and 4.05 mg kg^{-1}, respectively) were taken into account, the daily intake contribution of these metals was found to be 51.28 μg, 6.02 μg, and 1.215 mg for cadmium, mercury and copper, respectively. All the information would be helpful for human healthy. Among the tested cultivars, cvs. Jiahua, Wuyujing 3 and Chunjiang 012 had the lowest cadmium, mercury, and copper accumulation abilities in grains and are preferred candidates for cultivation and consumption.

Key words: Rice, cadmium, mercury, copper, food safety

INTRODUCTION

In the past several decades, rapid urban, industrial, and agricultural development, increasing reliance on agrochemicals, sewage irrigation, and mining and smelting activities in China have all led to agricultural soil contamination by heavy metals [1, 2]. Cadmium (Cd) contamination in soils is usually associated with other heavy metals as well, such as mercury (Hg) and copper (Cu)[3]. Numerous new techniques to remedy soils contaminated with heavy metals have been developed. However, these techniques are difficult to implement in contaminated farmland in developing countries because of their high costs and long durations. Recent findings of intra-specific variations in heavy metal accumulation in an increasing number of crops have led to the intense investigation of new strategies for screening, breeding, and using Cd pollution-safe cultivars [4].

Rice is more nutritious than many cereal grains. It is a staple in the diet of native peoples in china. One of the major pathways of adult exposure to the contaminants cadmium, mercury and copper is through the food chain [5]. The compositions of various metals in different food types of various countries have been the subject of many studies [3, 4, 6]. Chronic low-level intakes of heavy metals have damaging effects on human beings and other animals. In the Yangtse River Delta, where is highly developed region in China, it has been a common practice to cultivate and consume rice; however most of the paddy soil was polluted. The amount of heavy metal enter human diet from a crop depends on the amount of them accumulated in the portions that are consumed. And several accidents were caused by rice contented high heavy metals. Great differences between rice cultivars in their ability to absorb and accumulate heavy metals were extensively studied [4, 7]. However, there has been no report on the content of heavy metals in the rice grains cultivated and consumed in the region of the Yangtse River Delta.

Thus, the main aim of this study is to survey the concentrations of heavy metals in the commonly cultured rice cultivars in the Yangtse River Delta, and to estimate their contribution to the daily intake of the metals by the local inhabitant and potential risks, and further to identify rice cultivars which have inherently low grain heavy metals concentrations (food safety rice cultivars) and commend them to be cultured and consumed. This information would be helpful in determining which species are suitable and healthy.

EXPERIMENTAL SECTION

Soil： A paddy soil (0-25 cm), which was the representative soil in the Yangtse River Delta, was collected from the farm of Jiaxing, Zhejiang province. The soil sample was air-dried and passed through a 60 mesh before chemical analysis. Soil basic properties (Table 1) were determined according to the methods recommended by the Chinese Society of Soil Science [8]. Soil pH was measured in a 1:1 soil/water suspension with a combination electrode.

Table 1: Selected chemical properties of soil used in the experiment

Soil type	OM[a] (%)	CEC[b] (cmol kg^{-1})	Available N (mg kg^{-1})	Available P (mg kg^{-1})	Available K (mg kg^{-1})	pH	Cd (mg kg^{-1})	Cu (mg kg^{-1})	Hg (mg kg^{-1})
Paddy soil	5.19	14.2	128.4	17.2	126.4	5.89	0.43	33.01	0.47

[a] *organic matter*
[b] *cation exchange capacity*

Sample： 38 commonly cultured rice cultivars were collected from the delta of the Yangtse River. Among them 20 cultivars are japonica rice, and 18 are indica rice. They were sown in late May and transplanted at a 20 × 20 cm spacing at a rate of three seedlings per hill in late June at the experimental farm of Jiaxing, Zhejiang province from 2010-2012. Each cultivar was planted three replications with each an eight-row plot, 4 m long. The trail was managed according to locally recommended agronomic practices. At maturity, thirty spikes were harvested from each cultivar with similar mature date.

Determination of cadmium, copper and mercury： The microwave digestion of rice grain samples was used. A sample (1.000 g) was transferred to 100 ml Teflon beakers. A 10 ml volume of a freshly prepared mixture of concentrated nitric acid and perchloric acid (4:1, V/V) was added to each Teflon beaker. The mixture was submitted to a three-step program: 180W (3min), 360W (5min) and 180W (3 min). After digestion, the volume of the sample was made up to 25 ml with distilled water. Blank samples were prepared in the same ways as the sample, but omitting the sample. Cadmium and copper in the digested sample were determined by SolAAR-M6 FAAS. Mercury in the digested sample was determined by AFS-3100. Each sample solution was run in duplicate to ensure the reliability of the obtained results. Quality assurance was carried out on each batch of samples by the determination of Cd, Cu, Hg in certified reference materials (GBW 07310).

Data were analyzed with the SPSS 16.0 statistical software and EXCEL'2003 for Windows. Two significance levels, $p < 0.05$ and 0.01, were used in the present results.

RESULTS AND DISCUSSION

Soil basic properties and heavy metal concentrations： Table 1 shows the properties of the paddy soil. It was a blue purple clay soil with low pH. It also contained moderate levels of organic matter, cation-exchange capacity (CEC), nitrogen, Cd and Hg and a low level of Cu. So the paddy soil in this region was contaminated by cadmium and mercury. Elevated levels of heavy metals in soils are a result of industrial activities, atmospheric deposition and the land application of sewage sludge and fertilizer [9].

Cadmium, copper and mercury contents in rice grains： The wide variations among different rice cultivars in Cd, Hg and Cu concentrations of rice grains are listed in Tables 2. All samples have concentrations above the detection limits. For any given metal, a very significant difference was observed in the levels among the various rice cultivars. It is evident that the Cd, Hg and Cu contents in some rice grain are very high. Of the 38 cultivars, the mean Cd concentrations were 155.79 μg kg^{-1} ranged from 1.72 to 544.35 μg kg^{-1} (300-fold variation) in grain in the Yangtse River Delta. These values were close to the value 0.179 mg kg^{-1} reported by Buscema [10] and appreciably higher than 0.021 mg$^{\cdot}$ kg^{-1} reported by Bennetta *et al*. [11] in wild rice and Al-Saleh and Shinwari [12]. Figure 1 indicates the distribution of 38 cultivars in terms of Cd concentrations of rice grains. 34 cultivars (89.47 %) showed Cd concentrations ranging from 1 to 300 μg kg^{-1}. Only 4 cultivars (10.53 %) exhibited Cd concentrations higher than

300 µg kg^{-1}. The mean contents for mercury were 19.26 µg kg^{-1} ranged from 1.12 to 58.98 µg kg^{-1} (50-fold variation) in grains. These values were lower than that reported by Bennetta *et al*. [11] and higher than 0.003 mg kg^{-1} reported by Al-Saleh and Shinwari [12]. For Hg, 29 cultivars (76.32 %) showed Hg concentrations ranging from 1 to 30 µg kg^{-1}. Only 9 cultivars (23.68 %) exhibited Hg concentrations higher than 30 µg kg^{-1}. The mean contents for Cu were 3.83 mg kg^{-1} ranged from 1.81 to 6.54 mg kg^{-1} (3.5-fold variation) in grains.

Table 2: Concentration of cadmium, mercury and copper in rice grains

Type	Cultivar	Cd (µg kg^{-1})	Hg (µg kg^{-1})	Cu (mg kg^{-1})
Indica	Wufuxian	226.35 defg	8.10 mno	3.02 ijklmn
	Yang 9850	269.20 cde	36.45 e	5.20 b
	Nanjing 16	274.55 cd	27.39 g	3.67 efghijkl
	Zhenxian 866	544.35 a	58.98 a	4.14 cdefg
	K41	55.65 klmno	13.9 1jk	4.21 cdefg
	Zhou 903	114.40 ghijklmno	36.53 de	3.65 efghijkl
	Zhe 2	64.07 ijklmno	5.99 nop	3.87 defghij
	Fenyouzhao 11	79.40 ijklmno	21.58 h	3.37 ghijklm
	Zhe 733	69.62 ijklmno	38.03 cd	2.30 no
	Hang 931	148.53 fghijkl	2.45 rs	4.54 bcde
	Zhefu 802	127.43 fghijklmn	10.57 lm	4.04 cdefgh
	Zhongyouzhao 1	141.41 fghijklm	5.55 op	3.42 ghijklm
	Zhongdao 98186	125.01 fghijklmn	2.63 qrs	6.19 a
	Yuanfenzhaoxian	131.51 fghijklm	4.48 pqr	4.10 cdefgh
	Zhaoxiangxian	167.37 defghijk	6.48 nop	3.63 efghijkl
	Jia 948	144.31 fghijkl	14.23 ijk	4.99 bc
	Jiayu 293	157.04 efeghijkl	1.12 s	3.85 defghij
	Zhe 1	178.13 defghi	9.36 lm	2.84 lmn
	Zhongsi 3	353.05 bc	34.62 e	5.42 ab
	Qingliuai	25.93 mno	8.71 mn	4.78 bcd
Japonica	Wuyujing 7	351.85 bc	21.11 h	3.50 ghijkl
	Nanjing 40	1.72 o	31.57 f	3.15 hijklmn
	Suhujing	117.51 fghijklmno	15.25 ij	3.15 hijklmn
	Nanjing 41	231.95 def	8.38 mn	3.49 ghijkl
	Wuyujing 3	13.23 no	22.81 h	4.49 bcdef
	Jinqiu	175.11 defghij	15.37 ij	3.44 ghijkl
	Xiushui 11	59.05 jklmno	42.70 b	2.93 jklmn
	K12	72.47 ijklmno	40.04 bc	1.81 o
	Chunjiang 012	100.13 hijklmno	15.34 ij	3.02 ijklmn
	Zhenongda 104	46.95l mno	28.44 g	4.77 bcd
	Zhonghua	205.41 defgh	14.23 jik	6.54 a
	Chunjiang 026	127.53 fghijklmn	16.42 ij	3.57 fghijkl
	Chunjiang 25	105.71 hijklmno	16.94 i	3.26 ghijklmn
	Huangjin	204.62 defgh	14.58 ijk	2.84 klmn
	Xiushui 110	514.31 b	22.62 h	2.52 mno
	Chunjiang 016	180.75 defghi	41.68 b	4.07 cdefgh
	Zhejiang 1500	69.63 ijklmno	5.28 pq	3.96 defghi
	Jiahua	45.02l mno	11.95 kl	3.79 efghijk
AV		155.79±115.34	19.26±14.00	3.83±0.99
Range		1.72 -544.35	1.12-58.98	1.81- 6.54
CV		1.24	1.23	1.03

Copper is both essential element for plant growth and mobile within the plant, which probably explains the highest concentrations in rice seeds [11]. From the results, it can be noted that the levels of copper obtained in this study are slightly lower than those reported by Bennetta *et al*.[11]. In the case of Cu, 38 cultivars (100 %) showed Cu concentrations ranging from 0 to 10 mg kg^{-1}. The variations of the metal contents in those rice grains depend on not only the absorption capacity of each metal by the plant, which is determined to the nature of plant[13, 14], but also the heavy metal concentrations of soils. For instance, the Cd concentrations in brown rice ranged from 0.22 to 2.86 mg kg^{-1} when grown in highly Cd-contaminated soil (100 mg kg^{-1}) [13].

Pip found a significant inverse relationship between Cu and Cd in the samples that were analyzed [15]. Our experiments presented here showed that the accumulation of Cd in rice grains was positively correlated significantly with Hg, and that was no significant inverse relationships with Cu. However, there was significantly negative relationship between Hg and Cu (Table 4). The concentrations of trace metals in rice can be affected by genetic factors, as well as the source and form of the metal. These results imply that some interactions existed in absorption and translocation between the both, which is worthy of further investigation.

Table 4 shows the variations between rice types in terms of Cd, Hg and Cu concentration of brown rice. The differences in the average contents of Cd and Cu between the japonica and the indica were not significant while that of Hg was significant (Table 4). When the assayed values of the three elements of both rice grains, the average concentrations of Cd (156.82 μg kg^{-1}) and Cu (3.57 mg$^{\cdot}$ kg^{-1}) from the indica were approximately same as those from the japonica.

Table 3: Correlation coefficients between Cd, Hg and Cu in rice grain (38)

Element	Correlation coefficient (R)		
	Cd	Hg	Cu
Cd	1		
Hg	0.3018**	1	
Cu	-0.0759	-0.1577*	1

**, ** indicate the significance at the level of 0.05 and 0.01, respectively.*

Table 4: Variations in Cd, Hg and Cu accumulation of grain among rice types

	Types	Sample numbers	Hg (μg kg^{-1})	Cd (μg kg^{-1})	Cu (mg kg^{-1})
AV	Indica	20	21.37±15.98*	169.86±119.54	4.06±0.93
	Japonica	18	17.36±11.22	156.82±164.82	3.57±1.01
Range	Indica	20	1.12-58.98	25.93-544.35	2.30-6.19
	Japonica	18	5.28-42.70	1.72-514.31	1.81-6.54
CV	Indica	20	1.34	1.21	1.02
	Japonica	18	1.12	1.31	1.04

** indicates the significance at the level of 0.05.*

Food safety and total Cd, Hg, Cu intake： The present experiment showed that the average Cd concentrations in brown rice grown in the Yangtse River Delta were 1.56 times higher than the maximum safe intake levels (0.1 mg Cd kg^{-1}) in grains proposed by the FAO/WHO [16] (Table 2). And 68.42 % of them exceeded the maximum limit of Cd concentration (0.1 mg kg^{-1}) WHO (Table 5). The average concentrations of Hg and Cu in brown rice were close to or lower than the maximum safe intake levels. And 39.47 % of them were higher than the maximum limit of Hg (0.02 mg kg^{-1}). However, all rice had lower levels of Cu than the permissible value (10 mg kg^{-1}). From the result, the percentage of the indica, which Cd concentration exceeded the safe limit at the level of FAO, was higher than that of the japonica. As to Hg, however, the percentage of the indica was lower than that of the japonica.

It has been noted that the uptake and translocation of heavy metal to consumable parts of crops varied greatly with plant species and with cultivars within a species [17, 18]. The present study also showed a great difference in Cd, Hg and Cu concentrations of brown rice among the 38 rice cultivars grown in lightly contaminated soil. Morishita *et al*. showed a very wide variation among 56 rice cultivars of different types in Cd concentrations of brown rice, ranging from 2.1 to 73.6 ng g^{-1}, growing in a non-contaminated area [19]. The differences in seed Cd, Hg, Cu concentrations among plant species depend on the translocation of Cd from vegetative to generative plant parts [20].

Rice is one of the most traditional diets in china, especially in south of china. To calculate the total Cd, Hg, Cu intake, it is necessary to determine not only the Cd, Hg and Cu concentration in rice but also the mean daily rice consumption in the local region. In general it is not easy to estimate accurately the total Cd, Hg, Cu intake in each person. So we estimated the total Cd, Hg, Cu intake of each person based on the rice Cd concentration ingested and the history of residence for each person. If it is assumed people in the Yangzi River Delta may consume 300 g rice per day, calculated daily mean cadmium, copper and mercury intakes were 46.74 μg, 1.149 mg and 5.78 μg, respectively. Of the 38 tested rice grain samples, some indica rice had the much high cadmium and mercury contents. This is very disturbing because indica rice is the most popular rice in the Yangtse River Delta. It is worse considering to the mean daily Cd, Hg and Cu intake from foods other than rice. Our result indicates the concentrations of those heavy metals of brown rice may be reduced by more than 95% by selecting appropriate rice cultivars. It seems clear that human heavy metals intake from diets and health hazards can be reduced substantially by selecting and growing crop cultivars with a low heavy metals in grains.

Table 5: The numbers (percentage) of rice cultivars which Cd, Hg, Cu concentrations exceed the permissible value in food provided by FAO/WHO

Type	Number	Cd	Hg	Cu
All rice	38	26 (68.42 %)	15 (39.47 %)	0 (0)
Indica	20	15 (75 %)	7 (35 %)	0 (0)
Japonica	18	11 (61.11 %)	8 (44.44 %)	0 (0)

The numbers in bracket indicate distribution rate (%).

CONCLUSION

The concentrations of Cd, Hg and Cu in rice grains different among the 38 rice from the Yangtse River Delta and some rice grains are not suitable for human consumption. All these metals have toxic potential, but the detrimental impact becomes apparent only after decades of exposure. Therefore, restriction of the high-heavy metals rice grain consumption here and the establishment of a monitoring program should be considered in order to protect the residents from the potential of toxicity and to improve food safety. The japonica, especially jiahua, Wuyujing 3 and Chunjiang 012, should be cultured and consumed.

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