Strategies to Enable the Safe Use of Cadmium-Contaminated Paddy Soils in Southern China

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1 Introduction

With the rapid progression of industrialization, urbanization, and modern agriculture, large amounts of pollutants, especially heavy metals, are entering the soil in China's agricultural areas. According to the survey by the Ministry of Environmental Protection and the Ministry of Land Resources, 19.4% for the agricultural soils are contaminated based on China's soil environmental quality limits, cadmium being the primary contaminant. The total area of agricultural soils contaminated by cadmium is 10 million ha (7% of China's cultivated land) and is mostly distributed in the southern rice region (Ministry of Environmental Protection P. R. C. and Ministry of Land and Resources P. R. C. 2014). Cadmium in the soil might enter the food chain relatively easily by absorption into agricultural products and therefore poses a considerable threat to human health (Toppi and Gabbrielli 1999; Chen et al. 2016). An investigation from the Ministry of Agriculture indicated that over 10% of brown rice are Cd-contaminated (Li and Xu 2015).

More recently, as a result of the ever-increasing problem of agricultural Cd contamination, researchers in China and abroad have been studying the effectiveness of techniques such as agronomic regulation, in situ immobilization, soil washing and flushing, and electrokinetics (Li and Xu 2015; Zhu et al. 2012). The total area polluted by Cd is large and widely distributed, with varying degrees of pollution. In order to guarantee the security of the food supply and the quality of agricultural products of China, while also ensuring that the agricultural production on 1.8 billion ha of cultivated land does not simultaneously and abruptly stop, the only feasible way is to treat the issue of Cd contamination while maintaining

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production. In response to the seriousness of the problem of Cd contamination in China's southern rice paddies, our research team proposed a methodological philosophy of "clarify the problem, treat locally, strategize by zone, and proceed with caution." With this philosophy in mind, a system of techniques developed to treat the Cd-contaminated paddy soils while maintaining agricultural production. Thus, the aim of this study was to develop a model for the safe production of rice crops in slightly Cd-contaminated paddy soils in China. To achieve this aim, our study employed and investigated several methods in slightly contaminated paddies, such as the use of low-cadmium rice varieties, moisture management in the paddies, and in situ immobilization. The aim of these methods was to ensure the quality and safety of agricultural products without disrupting planting models.

2 Cultivation of Low-Cadmium Rice Varieties

Previous research has demonstrated significant differences in Cd accumulation among different rice varieties (Chen et al. 2016). Shi et al. (2009) planted 110 varieties of hybrid and super hybrid rice in slightly a Cd-contaminated paddy soil. Their research showed that Cd accumulation can differ by a factor of 14 among different rice varieties. Cao et al. (2014) studied Cd accumulation in 158 newly bred rice varieties. Their results showed that hybrid rice varieties are much more capable than conventional rice in terms of cadmium accumulation. However, there is a lack of data regarding which low-cadmium rice varieties are suitable for large-scale planting in the Cd-contaminated paddy soils of southern China. The present study collected a total of 473 rice varieties commonly grown in southern China (Table 1). All varieties were planted in a soil with a Cd concentration of 1.78 mg/kg and a pH of 4.72 to compare and analyze their Cd accumulation abilities.

Our results indicated that there was a large variation in Cd accumulation among the 473 popular rice varieties investigated in this study (Fig. 1). Brown rice variety *LIANG YOU* 616 had the highest cadmium content, reaching 6.39 mg/kg, 7.6 times higher than variety *JIN YOU* 268, which had the lowest cadmium content among the varieties tested. And rice varieties with the low-Cd accumulation were *JIN YOU* 268, *XIANG ZAO XIAN* number 32, *ZHU LIANG YOU* 189, *ZHU LIANG YOU* number 1, *CHUAN NONG YOU* 528, *SHUO FENG* number 2, *JIN YOU* 433, *Y LIANG YOU* 1998, *YOU* I651, and *ZHU LIANG YOU* 06. The Cd contents of the brown rice in these varieties were in the range of 0.84–1.29 mg/kg. These varieties could be used to mitigate the threat of Cd contamination in the paddy soils of southern China.

Table 1 Sources of rice varieties used to test Cd accumulation

Province	Number of varieties
Hunan	212
Fujian	21
Jiangxi	29
Yunnan, Guangxi	96
Zhejiang	67
Sichuan, Chongqing	48
Total	473

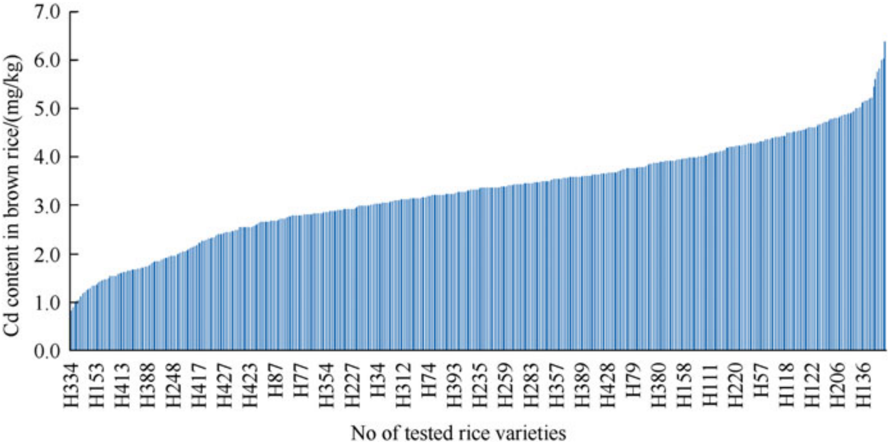

Fig. 1 Abilities of rice varieties from southern China to accumulate Cd

3 Water Management in Paddies

Moisture conditions in paddy soils affect the soil's redox potential. Moisture affects the pH of the soil, as well as the presence of iron and manganese oxides, thereby affecting the phytoavailability of the Cd in the soil (Zhu et al. 2012; Li and Xu 2015). Therefore, paddy testing was carried out in soil with Cd contents of 0.37 mg/kg, 0.63 mg/kg, and 0.88 mg/kg, with pH levels ranging from 5.3 to 5.5. Our results showed that, compared to conventional water management, the use of flooding during the entire growth period could, to a certain extent, reduce the cadmium content of the brown rice (Fig. 2). The Cd content of early rice was reduced by 16.9–30.4%, while the cadmium content of later rice was reduced by 13.9–23.3%. In soil with a Cd content of 0.37 mg/kg, this technique basically guaranteed that the Cd content of early and late rice could be kept to below the national contaminant limits in food crops of 0.2 mg/kg (GB2762—2012). In soil with a Cd content of 0.63 mg/kg, the Cd content of early rice fell within the standard of 0.2 mg/kg. However, when the Cd content of the soil was 0.88 mg/kg, the Cd contents of both early and late rice failed to meet this standard.

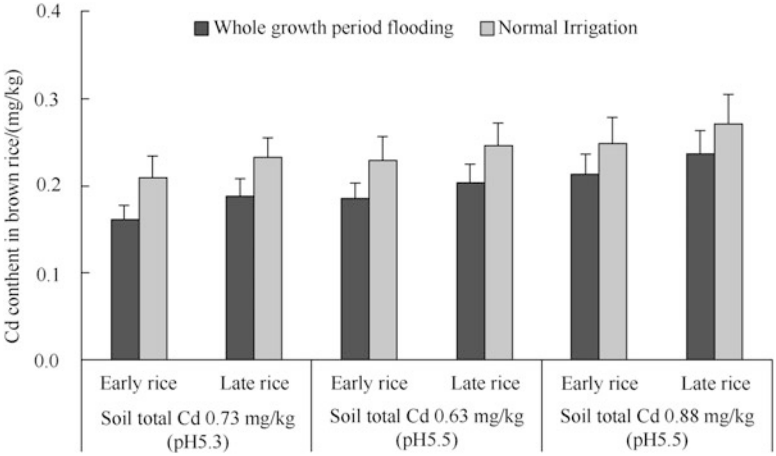

Fig. 2 Effect of water management on Cd content of rice

Water management with controlled flooding during the entire growth period is an effective technique to reduce Cd content in rice grown in Cd-contaminated paddy soils. However, this method requires a source of abundant, clean water for irrigation, as there is a risk of side effects such as gleization of the soil, which can lead to increased arsenic content in the rice. The method must be combined with appropriate sun drying of the paddy.

4 In Situ Immobilization Techniques

In recent years, the in situ immobilization of high-Cd soil has been gaining attention as an economical and effective remediation measure (Feng et al. 2013). Commonly used amendments can essentially be divided into lime substances, phosphate substances, biochar, substances containing iron and manganese, and organic substances. By increasing the pH of the soil, thereby causing Cd to coprecipitate or to be absorbed or chelated, the mobility and phytoavailability of Cd in the soil is reduced, thus reducing the content of Cd in brown rice. In order to ensure the effectiveness of this technique, and to keep the price of amendment low, we mainly selected agricultural waste products as raw materials for amendments. Continuous, in situ immobilization experiments were developed in high-Cd soils over the course of several growing seasons. The soil used in the experiment was reddish-yellow mud from red quaternary clay. See Tables 2 and 3 for the basic properties of the soil and the heavy metals content of the amendments. Eight different treatments were established: control (CK) with no amendments, lime (L) (90 g/m^2 of quicklime), slag (S) (1,125 g/m^2), bagasse (B) (1,125 g/m^2), lime+slag (LS), lime+bagasse (LB), slag+bagasse (SB), and lime+slag+bagasse (LSB). All amendment materials

Table 2 Select physical and chemical properties of tested soil

Properties	Values
pH	5.72
Organic matter content (g/kg)	34.2
Total N (g/kg)	1.84
Available P (m-g/kg)	26.9
Available K (m-g/kg)	80
Cation exchange capacity (CEC, cmol/kg)	10.1
Clay content (%)	48.9
Total Cd (m-g/kg)	1.2
$CaCl_2$-extractable Cd (m-g/kg)	0.053

Table 3 Heavy metals contents and pH of amendments

Amendments	pH	Heavy metals (mg/kg)					
		Cd	Cu	Cr	Pb	Zn	Ni
Lime	12.75	0.24	1.17	1.00	0.98	5.82	1.62
Bagasse	10.14	0.76	21.87	2.81	4.42	47.68	1.06
Slag	9.08	1.20	76.12	4.19	2.03	322.51	9.19

were raked into the fields by hand 7 days prior to transplanting in the first season (2013 late rice). The rice was managed using conventional methods. Rice shoot and soil surface samples were taken at harvest time.

4.1 Effects of Amendments on Soil pH and $CaCl_2$-Extractable Cd

A three-way analysis of variance (ANOVA) indicated that the application of lime, slag, and bagasse significantly increased soil pH ($p < 0.05$) and that the effects were sustained for at least three harvest seasons (Table 4). In the late rice season of 2013 (first season), the soil pH of the control treatment (CK) was 5.72, which increased to 5.93 and 6.17 in the early (second season) and late (third season) harvest seasons of 2014, respectively. After the application of the different amendments, the soil pH significantly increased by 0.48–1.37 units ($p < 0.05$) in the first season. While no significant difference in soil pH were observed for the three amendments applied as single treatments ($p > 0.05$), the pH of the soils with amendments applied as mixtures were higher than in soils where the three amendments were applied alone. Similar increases in soil pH resulting from the different amendments were also observed in both 2014 harvest seasons.

The $CaCl_2$-extractable Cd in the CK soil slightly decreased from 0.053 to 0.042 mg/kg during the three harvest seasons (Table 4). A three-way ANOVA demonstrated that treatments L, S, and B significantly decreased the $CaCl_2$-extractable Cd, while this interaction was only observed in S × B in the first rice season

Table 4 Effects of amendments on soil pH and $CaCl_2$-extractable Cd

	2013-late rice		2014-early rice		2014-late rice	
Treatments	pH	$CaCl_2$-extractable Cd mg/kg	pH	$CaCl_2$-extractable Cd mg/kg	pH	$CaCl_2$-extractable Cd mg/kg
CK	5.72 ± 0.05 d	0.053 ± 0.003 a	5.93 ± 0.03 d	0.050 ± 0.02 a	6.17 ± 0.04 d	0.042 ± 0.007 a
L	6.25 ± 0.16 c	0.026 ± 0.007 b	6.21 ± 0.06 cd	0.032 ± 0.003 b	6.47 ± 0.11 cd	0.026 ± 0.005 bc
S	6.56 ± 0.17 bc	0.022 ± 0.003 b	6.62 ± 0.07 ab	0.016 ± 0.003 cd	6.63 ± 0.14 bc	0.016 ± 0.003 cd
B	6.20 ± 0.10 c	0.028 ± 0.003 b	6.22 ± 0.09 cd	0.033 ± 0.005 b	6.38 ± 0.06 cd	0.031 ± 0.005 ab
LS	6.93 ± 0.20 ab	0.005 ± 0.001 c	6.81 ± 0.11 a	0.015 ± 0.001 cd	7.01 ± 0.10 a	0.008 ± 0.002 d
LB	6.56 ± 0.12 bc	0.020 ± 0.005 b	6.48 ± 0.13 bc	0.025 ± 0.005 bc	6.63 ± 0.08 bc	0.017 ± 0.003 cd
SB	7.09 ± 0.10 a	0.004 ± 0.001 c	6.88 ± 0.16 a	0.015 ± 0.003 cd	6.92 ± 0.06 ab	0.011 ± 0.000 d
LSB	7.03 ± 0.18 a	0.007 ± 0.003 c	6.80 ± 0.10 a	0.013 ± 0.002 d	7.01 ± 0.18 a	0.010 ± 0.005 d

Data represent the mean ± SE, $n = 3$

and in L × S and L × B in the second rice season ($p < 0.05$). Compared with the control treatment, the application of lime alone (L) significantly reduced the $CaCl_2$-extractable Cd by 51.2%, 36.1%, and 38.2% in the first, second, and third rice seasons, respectively. Similar to treatment L, the application of slag (S) and bagasse (B) alone significantly reduced the $CaCl_2$-extractable Cd 59.1–67.0% and 26.4–47.4%, respectively, during the three rice seasons. Moreover, the application of LS, LB, SB, and LSB significantly reduced the $CaCl_2$-extractable Cd in soil by 69.8–89.9%, 49.4–61.4%, 69.2–93.3%, and 73.3–86.6%, respectively, during the three rice seasons. Generally, the three amendments successfully reduced the $CaCl_2$-extractable Cd in soil in the following order: $S > L \approx B$, where the mixtures were more effective than the three amendments alone.

4.2 Effects of Amendments on Cd Uptake

A three-way ANOVA indicated that L significantly affected Cd accumulation in brown rice in the first and third rice seasons, S significantly affected Cd accumulation in the second and third rice seasons, and B significantly affected the Cd accumulation in only the first rice season ($p < 0.05$) (Table 4). In the CK, the Cd contents of brown rice were 1.42, 0.50, and 1.44 mg/kg for the late rice season in 2013 and the early and late rice seasons in 2014, respectively (Fig. 3). Compared with the CK, the application of L, S, and B alone decreased the Cd contents of brown rice by 42.3%, 15.8%, and 40.8%, respectively, in the first rice season. Similarly, the Cd contents of brown rice decreased by 49.8%, 18.9%, and 10.1% after the application of L, S, and B alone, respectively, in the third season. However,

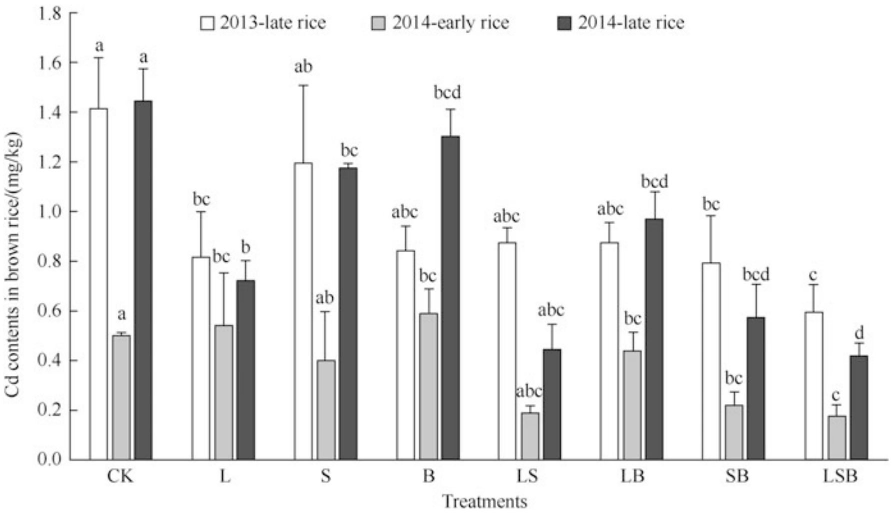

Fig. 3 Effect of amendments on the Cd content of brown rice

the application of L and B alone increased the Cd contents of brown rice by 8.1% and 18.1%, respectively, compared to the CK in the second rice season. Correspondingly, a steady decrease in the Cd content of brown rice was observed with the application of the mixtures, with the exception of the SB treatment. During the three rice seasons, the application of LS, SB and LSB reduced the Cd contents of brown rice 38.3–58.3%, 55.6–65.0%, and 60.0–70.9%, respectively.

5 Techniques for the Safe Use of Slightly Cd-Contaminated Paddy Soils: Model Construction and Application

Although the techniques described above can effectively decrease the accumulation of Cd in rice, they have a very limited range of appropriate uses. We have established that the use of these techniques effectively guarantees safe production in slightly Cd-contaminated paddy soils. Next, the study combined the use of low-cadmium rice varieties (V), flood irrigation (I), lime to increase soil pH (P), and the use of amendments or foliar application of trace elements (n) to create a model of VIP and VIP+*n* techniques. Experiments and demonstrations were developed in Changsha, Zhuzhou, and Xiangtan of Hunan Province in China.

A total of 48 test sites were selected for 2 growing seasons in slightly (soil total Cd contents $\leq$0.6 mg/kg), moderately (0.6 mg/kg $\leq$ soil total Cd content $\leq$1.0 mg/kg), and heavily (1.0 mg/kg $\leq$ soil total Cd content) Cd-contaminated paddy soils. There were 32 slightly contaminated sites, 7 moderately contaminated sites, and 9 heavily contaminated sites. There was one control group at each site using local rice varieties and conventional irrigation. VIP and VIP+*n* treated test and demonstration sites were at least 5 ha in area.

Low Cd-accumulation rice varieties (V) comprised the following five early rice varieties: *XIANG ZAO XIAN* number 32, *XIANG ZAO XIAN* number 45, *ZHONG JIA ZAO* 17, *ZHU LIANG YOU* 819, and *ZHU LIANG YOU* 189. There were also three low Cd-accumulation varieties of late rice: *XIANG WAN XIAN* number 12, *XIANG WAN XIAN* number 13, and *JIN YOU* 59.

Water management included conventional irrigation (i.e., sun drying the paddies during tilling and ripening stages) and the flood irrigation technique (I) (i.e., maintaining a layer of water throughout the development period). Lime was used at 750–1,800 kg/ha depending on soil quality and pH value (P). There were five soil conditioners used: *XIANG YU FENG*, *SHI LI KANG*, *ZHONG KE*, *XING WANG HONG*, and *MATA*. Five organic fertilizers were used, such as *JIN KUI ZI* microbial agents. In addition, six foliar resistance control agents were used, such as *WO NONG* and *ZHONG KE* (+*n*). Methods and quantities used were in accordance with manufacturers' instructions.

Results from demonstration experiments in slightly and moderately Cd-contaminated paddy soils with over two seasons showed that, when using none of these techniques and growing local rice varieties, the pH values of average early rice soil were 5.70 and 5.28, respectively. Additionally, the average available Cd content in the soils was 0.37 mg/kg and 0.52 mg/kg, respectively, the average Cd content in rice brown was 0.26 mg/kg and 0.53 mg/kg, and the proportion of brown rice that met national contaminant limits in food crops was 23.3% and 16.0%. The available Cd content in soils for the late rice season was 0.56 mg/kg and 0.42 mg/kg, the average soil pH was 5.86 and 5.43, and the Cd content in rice brown was 0.43 mg/kg and 0.57 mg/kg. The proportion of rice that met national contaminant limits in food crops was 30.7% and 10.3% (Table 5 and Fig. 4).

In slightly and moderately contaminated fields, the use of VIP techniques increased the pH of soil for early rice season by 0.05 and 0.03 units, respectively, compared with the control group, while the average available Cd content of the solid decreased by 4.6% and 34.9%. Additionally, the average Cd content of brown rice decreased by 34.3% and 47.1% in slightly and moderately contaminated fields, respectively, and rice that met the national contaminant limits in food crops increased to 74.7% and 47.8%. The average pH of soil for late rice season increased slightly, the average available Cd content of the soil decreased, and the average Cd content of brown rice decreased by 37.1% and 50.7%. In addition, the proportion of rice that met the national contaminant limits in food crops increased to 70.0% and 43.3%. Using VIP+*n* techniques in slightly and moderately contaminated soils, the average soil pH increased by 0.15 and 0.10 units, respectively. The average effective cadmium content in the soil decreased by 13.5% and 19.4%, the average Cd content of brown rice decreased by 48.4% and 50.2%, and the proportion of brown rice that met the national contaminant limits in food crops was 80.0% and 52.7%. The average pH of soil for late rice season increased by 0.26 and 0.33 units. The average available Cd content of the soil decreased, the average cadmium content of brown rice decreased by 55.6% and 60.5%, while the proportion of rice that met the national contaminant limits in food crops was 78.1% and 50.0%. In heavily contaminated paddy soils, the changes in soil pH and the available Cd content of the soil were similar to slightly and moderately contaminated paddy soils. The Cd content in brown rice decreased by 23.3–51.4%. However, less than 12% of the brown rice met the national contaminant limits in food crops. In conclusion, the VIP and VIP+*n* models guarantee the production of rice products that meet the national contaminant limits in food crops in slightly Cd-contaminated paddy soils. In moderately Cd-contaminated paddy soil, these techniques are useful in reducing Cd content; however, the proportion of rice that meets the national contaminant limits in food crops should be further improved for increased safety. These methods are not very effective in heavily Cd-contaminated paddy soils.

Table 5 Effect of VIP and VIP+*n* on soil pH, available Cd and brown rice Cd contents

		Early rice						Late rice					
		DTPA-Cd in soil		Soil pH		Cd in brown rice		DTPA-Cd in soil		Soil pH		Cd in brown rice	
Contamination level	Treatment	Mean mg/kg	Reduction %	Mean	Increase	Mean mg/kg	Reduction %	Mean mg/kg	Reduction %	Mean	Increase	Mean mg/kg	Reduction %
Slightly ($n = 32$)	CK	0.37	–	5.7	–	0.26	–	0.56	–	5.86	–	0.43	–
	VIP	0.36	4.6	5.74	0.05	0.17	34.3	0.55	–	5.89	0.03	0.27	37.1
	VIP+*n*	0.32	13.5	5.85	0.15	0.13	48.4	0.56	–	6.12	0.26	0.19	55.6
Moderately ($n = 7$)	CK	0.52	–	5.28	–	0.53	–	0.42	–	5.43	–	0.57	–
	VIP	0.34	34.9	5.31	0.03	0.28	47.1	0.42	–	5.52	0.09	0.28	50.7
	VIP+*n*	0.42	19.4	5.39	0.1	0.26	50.2	0.42	–	5.76	0.33	0.23	60.5
Heavily ($n = 9$)	CK	1.01	–	5.48	–	0.87	–	0.64	–	5.56	–	0.94	–
	VIP	0.91	9.9	5.51	0.04	0.67	23.3	0.62	–	5.77	0.21	0.56	40.4
	VIP+*n*	0.76	24.9	5.62	0.15	0.62	28.9	0.54	15.4	5.82	0.26	0.46	51.4

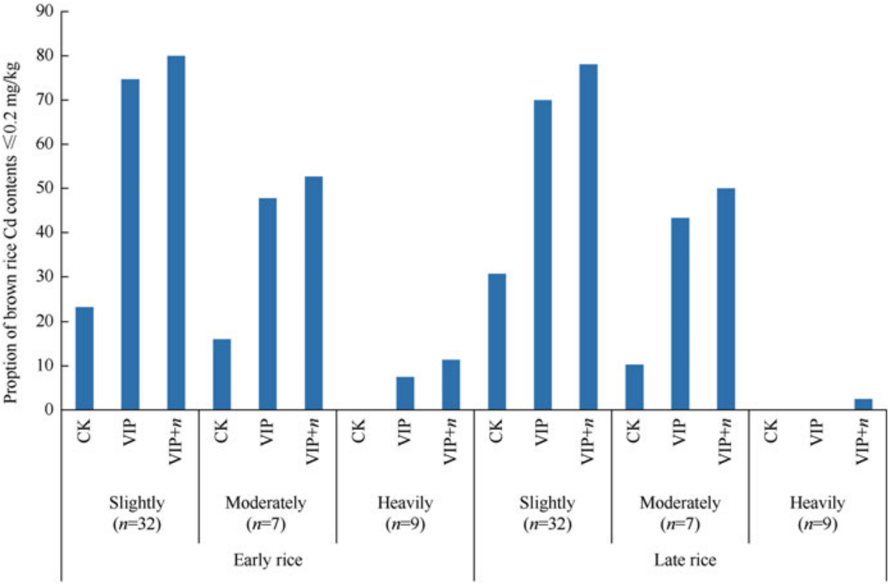

Fig. 4 Proportions of rice crops meeting the national contaminant limits in food crops used the VIP and VIP+*n* techniques

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