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Effects of several amendments on rice growth and uptake of copper and cadmium from a contaminated soil

LI Ping[1,2], WANG Xingxiang[1,*], ZHANG Taolin[1], ZHOU Dongmei[1], HE Yuanqiu[1]

1. Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China. E-mail: pli@issas.ac.cn
2. Graduate School of the Chinese Academy of Sciences, Beijing 100049, China

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Abstract

Heavy metals in variable charge soil are highly bioavailable and easy to transfer into plants. Since it is impossible to completely eliminate rice planting on contaminated soils, some remediation and mitigation techniques are necessary to reduce metal bioavailability and uptake by rice. This pot experiment investigated the effects of seven amendments on the growth of rice and uptake of heavy metals from a paddy soil that was contaminated by copper and cadmium. The best results were from the application of limestone that increased grain yield by 12.5–16.5 fold, and decreased Cu and Cd concentrations in grain by 23.0%–50.4%. Application of calcium magnesium phosphate, calcium silicate, pig manure, and peat also increased the grain yield by 0.3–15.3 fold, and effectively decreased the Cu and Cd concentrations in grain. Cd concentration in grain was slightly reduced in the treatments of Chinese milk vetch and zinc sulfate. Concentrations of Cu and Cd in grain and straw were dependent on the available Cu and Cd in the soils, and soil available Cu and Cd were significantly affected by the soil pH.

Key words: heavy metals; amendment; bioavailability; uptake; rice

Introduction

Heavy metal contamination in soil is a major problem for the environmental quality of the world (Purves, 1985; Yoon *et al*., 2006; Makino *et al*., 2006). It is also a serious problem in China, and has become increasingly serious with the development of mine exploration, metallurgy industry, paint pigments, and irrigation of wastewater. Nearly 2.0×10^7 hm^2 of cultivated land of China is contaminated with heavy metals (Sun, 2004), and this includes 2.8×10^5 hm^2 farmland contaminated by Cd (Cao *et al*., 1999). Heavy metal contamination not only degrades the quality of soil, aquatic and atmospheric environment, but also affects crop growth (Verma and Dubey, 2001); it even enters the agricultural food chain through uptake of heavy metal naturally in soil by plants and then causes serious problems to human health (Adriano, 1992). According to the tolerance limits of heavy metal in foods (MHC, 1994), 1.46×10^6 t crop in China exceeds the tolerance limit of Cd concentration in foods every year (Cao *et al*., 1999). Therefore, the remediation of heavy metal contaminated soils and food safety receives great attention (Wang, 1997).

The remediation techniques of heavy metals in soils include physical remediation, chemical remediation, phytoremediation, and agro-ecological engineering techniques (Chen *et al*., 1999; Chen, 2000). As the technique adopted extensively, chemical remediation stabilized heavy metals by adding some nontoxic materials into soils. Several researches indicated that the uptake of heavy metals by plants can be influenced by soil pH (Eriksson, 1989), soil organic matter content (McGrath *et al*., 1988), plant species (Bingham *et al*., 1979), clay mineral, sesquioxide content, fertilizer practices, and seasonal influences (Oliver *et al*., 1994).

The application of alkaline substances such as lime (Albasel and Cottenie, 1985), fly ash (Su and Wong, 2003), calcium carbonate, and manganese oxide (Chen *et al*., 2000) has successfully mitigated soil heavy metal contamination, and significantly reduced the contents of available heavy metals in soils, as well as the uptake by plants, mostly due to the increase of the soil pH. Organic materials such as green manure, animal excrement, and peat can also effectively remedy heavy metal contaminated soil by transforming heavy metals from soluble and exchangeable fractions to fraction associated with organic matter (OM), carbonates fraction, and residual fraction, which are unavailable to plants (Shuman, 1999; Walker *et al*., 2003). Furthermore, enhancing one heavy metal element may reduce the uptake of another heavy metal element by plants because of the competition between them. For example, the application of zinc fertilizer reportedly reduced Cd uptake by soybean shoot (Haghiri, 1974) and wheat grain (Oliver *et al*., 1994).

Variable charge soil, a dominating soil type in tropical and subtropical regions, is generally a highly weathered

* Corresponding author. E-mail: xxwang@issas.ac.cn.

soil with low fertility, low pH, and low effective cation exchange capacity. The hilly red soil region in southeastern China covers a total area of 1.13×10^6 km^2, and is an important rice production base in China. However, series of soil degradation such as soil pollution and soil erosion, have greatly affected the environment and the agricultural development of this region. According to the results of evaluation with integrated contaminative index, 69% of soil samples collected from the area of mine exploration, metallurgy industry, irrigation of wastewater in Jiangxi, Hunan, Fujian, and Guangdong Provinces were contaminated by heavy metals, and severe Cd pollution was found in some places of Jiangxi Province (Zhao, 2002). Heavy metals in variable charge soil are highly bioavailable and easy to transfer into plants owing to the low pH and low effective cation exchange capacity of the soil; therefore, it is important to develop some remediation techniques to decrease their bioavailability and uptake by plants.

The objective of this study was to investigate the effects of several amendments such as limestone, calcium magnesium phosphate, calcium silicate, Chinese milk vetch, pig manure, peat, and zinc sulfate on the bioavailability (extracted by 0.01 mol/L $CaCl_2$) and the uptake of Cu and Cd by rice in a paddy soil that was contaminated with Cu and Cd in central subtropical China.

1 Materials and methods

1.1 Soil samples

Soil samples were collected from the surface layer (0–20 cm in depth) of a paddy field located in Sumen Village, Binjiang County, Guixi City, Jiangxi Province, central subtropical China (28°20.307′N and 117°14.133′E). About 260 hm^2 paddy fields have been contaminated with Cu and Cd by sewerage from an adjacent smelting factory for more than 20 years (Hu *et al*., 2004). The paddy soil was developed from red sandstone with 13.0% clay, 40.5% silt, and 46.5% sand, and the main properties of soil are shown in Table 1. The total concentrations of Cu and Cd significantly exceed the environmental quality standard for agricultural soils (Cu 50 mg/kg and Cd 0.3 mg/kg in GB 15618-1995) issued by State Environmental Protection Administration of China. Unfortunately, rice is still planted on the contaminated soils by local farmers due to the drive of compensation mechanism and poverty.

1.2 Experimental design

The soil samples were air-dried and passed through a 4-mm sieve prior to the greenhouse pot experiment. The experiment was performed in fifteen treatments and four replicates per treatment (Table 2). Each treatment applied chemical fertilizers at the amount equivalent to N 150.75 kg/hm^2 as urea, P 38.25 kg/hm^2 as KH_2PO_4, K 150.75 kg/hm^2 as KH_2PO_4 and KCl, mixed with 7.5 kg air-dried soil thoroughly. The soil samples were then placed in plastic pots (23 cm in height and 31 cm in diameter). The amendments were also air-dried and ground to pass through a 2-mm mesh sieve, and were then applied as designed and mixed with the soils samples thoroughly. Among these amendments, limestone, Chinese milk vetch, and pig manure were from a local village; calcium magnesium phosphate (Ca-Mg-P fertilizer) was from Yingtan Yifeng Phosphate Fertilizer Co., Ltd., China; silicon fertilizer ($CaSiO_3$) was from Sinopharm Chemical Reagent Co., Ltd., China; peat was from Jiamushi Nongyou Peat Co., Ltd., China; and zinc fertilizer ($ZnSO_4 \cdot 7H_2O$) was from Shanghai Meixing Chemical Engineering Co., Ltd., China. The chemical properties of the amendments are given in Table 3.

After the application of chemical fertilizers and amendments, the soil mixtures in the pots were covered with 5 cm water above soil surface for 2 d, and seedlings of rice named Denong 108 (*Oryza sativa* L.) were transplanted into the pots with a density of two seedlings per pot on 24 July, 2006. The pots were kept in a greenhouse with a natural day/night regime and watered as required. Urea was applied as top fertilization at the amount of 30.15 kgN/hm^2 for all treatments on 22 August, 2006, and the rice was harvested on 14 November, 2006.

1.3 Soil and plant analysis

Prior to starting the greenhouse pot experiment, the pH and total contents of heavy metals in the contaminated

Table 1 Chemical properties of soil samples

pH	Organic matter (g/kg)	Total N (g/kg)	Total P (g/kg)	Total K (g/kg)	Total Cu (mg/kg)	Total Cd (mg/kg)	Total Zn (mg/kg)
4.51	26.5	1.68	0.35	10.96	1,073	6.79	71.1

Table 2 Experimental design for the treatments of the pot experiment

Treatment	Material added	Amount (g/pot)	Treatment	Material added	Amount (g/pot)
Control	Only soil and fertilizer		CMV2	Chinese milk vetch	30
L1	Limestone	5	PM1	Pig manure	10
L2	Limestone	15	PM2	Pig manure	30
PF1	Ca-Mg-P fertilizer	5	PE1	Peat	30
PF2	Ca-Mg-P fertilizer	15	PE2	Peat	90
Si1	$CaSiO_3$	5	Zn1	$ZnSO_4 \cdot 7H_2O$	0.8295
Si2	$CaSiO_3$	15	Zn2	$ZnSO_4 \cdot 7H_2O$	2.4885
CMV1	Chinese milk vetch	10			

1 and 2 indicate lower and higher rates of amendments application.

Table 3 Chemical properties of amendments (dry weight basis)

Amendment	pH	Total C (g/kg)	Total N (g/kg)	Total Cu (mg/kg)	Total Cd (mg/kg)	Total Zn (mg/kg)
Limestone	12.38	Nd	Nd	6.52	8.60	20.8
Ca-Mg-P fertilizer	7.36	Nd	Nd	1310	4.81	1076
Silicon fertilizer	10.85	Nd	Nd	0.57	7.58	5.11
Zinc fertilizer	4.23	Nd	Nd	0.31	0.65	Nd
Chinese milk vetch	6.11	441	28.2	16.4	0.42	Nd
Pig manure	7.65	185	21.2	725	4.11	1417
Peat	4.03	322	22.0	13.8	1.94	44.8

Nd indicates not detected.

soil and amendments were measured. Organic matter, total N, P, and K of the soil, and total C and N of the organic amendments were also determined. The pH of the contaminated soil, Ca-Mg-P fertilizer, zinc fertilizer, pig manure, and peat were measured using a pH glass electrode in H_2O at a water:solid ratio of 2.5:1. The pH of limestone, silicon fertilizer, and Chinese milk vetch was measured at water:solid ratios of 5:1, 5:1, and 10:1, respectively. Chinese milk vetch was digested with concentrated HNO_3 and H_2O_2, while soil and others amendments were digested with concentrated HNO_3, HF, and $HClO_4$ (Lu, 2000), and then the total concentrations of Cu, Cd, Zn in the digested solutions were determined by an atomic absorption spectrometer (AAS) (Hitachi 180, Japan).

Organic matter of the soil was determined by potassium dichromate oxidation method. Total N was determined by semimicro-Kjeldahl method, after the soil was digested by $HClO_4$ and HF. Total P was determined by acidic molybate-ascorbic acid blue color method and total K was determined by the flame photometry method. Total C and total N of Chinese milk vetch, pig manure, and peat were determined by the potassium dichromate oxidation-sulfuric acid method and the semimicro-Kjeldahl method, respectively (Lu, 2000).

On the day of rice harvest, the soil pH was determined by an *in-situ* IQ150 pH Meter (Spectrum Technologies Inc., USA). Grain, straw, and root of the rice were collected and washed in deionized water, oven-dried at 70°C, and weighed. The samples of grain and straw were ground in a stainless steel mill and digested with concentrated HNO_3 and H_2O_2, and then the concentrations of Cu and Cd were measured by AAS. The soil was air-dried and passed through a 2-mm sieve after rice was harvested, and then the available Cu and Cd were extracted by 0.01 mol/L $CaCl_2$ (Spark, 1996) and determined by AAS.

1.4 Statistical analysis

All the data were statistically analyzed using one-way ANOVA at a significance level of $P < 0.05$ and $P < 0.01$ with SPSS 13.0 software. Duncan test was used to detect the significant differences between means of different treatments.

2 Results and discussion

2.1 Effects of amendments on soil pH and heavy metal bioavailability

The concentrations of available Cu and Cd and the pH values of the soils are shown in Table 4. The results showed that the soil pH was increased significantly and the increase of soil pH was significantly consistent with the increasing rates of amendments application except for zinc fertilizer. Owing to the strong alkalinity of limestone, the limestone treatments raised the soil pH by 1.60 unit for the lower rate and 2.45 unit for the higher rate, and the increases were the highest among all amendments treatments. Ca-Mg-P fertilizer and silicon fertilizer also increased the soil pH by 0.66–1.49 unit. For the treatments of pig manure applied at lower and higher rates, the soil pH was increased by 1.27 and 1.72 unit, respectively. This may be attributed to the release of NH_4^+ in the process of decomposition of pig manure (Zhang *et al.*, 2001). Application of Chinese milk vetch also increased the soil pH by 1.13 unit for the lower rate and 1.52 unit for the higher rate. These results were similar to the results reported by Chen and Zheng (1989). Chen *et al.* (2001) found a slight increase in the soil pH (0.2 unit) when a soil contaminated with Zn, Pb, and Cd was amended with peat. In this study, 0.50–0.74 unit increase of soil pH was also observed in peat treatments, although the pH value of peat was only 4.03, which may be partially due to the difference in the sampling and analytical methods (soil pH was determined *in-situ* on the day of rice harvest in our experiment). The results also showed that application of zinc fertilizer had no significant effect on the soil pH. The soil pH values at the two rates of treatments of different amendments followed the order: limestone > pig manure > Chinese milk vetch > silicon fertilizer > Ca-Mg-P fertilizer > peat > zinc fertilizer > control. For the treatments of the same amendment

Table 4 Soil pH and concentrations of available Cu and Cd in soil in different treatments

Treatment	pH	Cu (mg/kg)	Cd (mg/kg)
Control	4.02 g	339 a	2.39 a
L1	5.62 b	51.8 h	1.69 ef
L2	6.47 a	14.1 i	0.96 h
PF1	4.68 f	273 b	2.16 b
PF2	5.14 de	206 c	1.96 c
Si1	5.00 e	149 d	1.94 c
Si2	5.51 bc	89.2 ef	1.74 def
CMV1	5.15 de	104 e	1.91 c
CMV2	5.54 bc	62.9 gh	1.71 def
PM1	5.29 cd	81.1 fg	1.78 de
PM2	5.74 b	22.4 i	1.40 g
PE1	4.52 f	99.0 ef	1.84 cd
PE2	4.76 f	45.2 h	1.63 f
Zn1	4.12 g	326 a	2.31 a
Zn2	4.10 g	324 a	2.26 ab

Data are expressed as mean values, and the means with the same small letter in each column are not significantly different at $P < 0.05$.

material, a higher rate resulted in a significantly higher soil pH than a lower rate, except for the treatments of peat and zinc fertilizer.

The concentrations of available Cu and Cd in the soils decreased consistently with increasing rates of amendments application (Table 4), suggesting that these amendments reduced the bioavailability of Cu and Cd. Compared with the control, the application of 5 g inorganic amendments such as limestone, Ca-Mg-P fertilizer, and silicon fertilizer lowered the concentrations of available Cu by 84.7%, 19.4%, 56.0%, and the available Cd by 29.3%, 9.4%, 18.8%, respectively. However, only slight decreases in the concentrations of available Cu and Cd (3.1%–5.2%) were observed in the treatments of zinc fertilizer. The application of organic amendments also reduced the soil available Cu and Cd. For example, application of 10 g pig manure and Chinese milk vetch and 30 g peat lowered the concentrations of available Cu by 76.1%, 69.3%, 70.8%, and available Cd by 25.7%, 19.9%, 23.0%, respectively. In general, the concentrations of available Cu and Cd at two rates of treatments of different amendments followed the common order: limestone < pig manure < peat < Chinese milk vetch < silicon fertilizer < Ca-Mg-P fertilizer < zinc fertilizer < control, which reversed the order of the soil pH except for peat treatment. It can also be concluded that a higher rate treatment usually resulted in a significant lower concentration of available Cu and Cd than the lower rate treatment of the same amendment except for zinc fertilizer.

Soil available Cu and Cd were significantly affected by the soil pH (Fig.1), and the correlation between them can be described by the following regression equations (Eq.(1)):

$$\begin{aligned}&\text{For Cu:}\\&\quad Y = -139X + 849 \;\; (r = -0.82,\; P < 0.01)\\&\text{For Cd:}\\&\quad Y = -0.486X + 4.30 \;\; (r = -0.86,\; P < 0.01)\end{aligned} \tag{1}$$

where, Y represents the concentration of available Cu or Cd in soil (mg/kg), X represents the soil pH. Several studies have proved that the soil pH is an important factor controlling the mobility of heavy metals in soils (Wallace *et al*., 1974; Jackson and Miller, 2000).

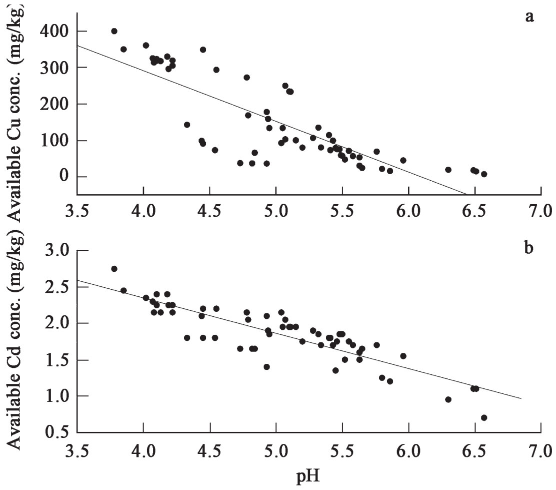

Fig. 1 Correlations between the concentrations of available Cu (a) and Cd (b) in soil and the soil pH.

Besides the soil pH, there are other factors that may also affect the bioavailability of heavy metals in soils. The properties of inorganic amendments as well as the undergoing chemical reaction were related to the decrease in the available Cu and Cd in the soil. For example, OH^- that is released by the dissolution of limestone can form CO_3^{2-} with CO_2, and then CO_3^{2-} reacts with Cu^{2+} and Cd^{2+} to form $CuCO_3$ and $CdCO_3$, which are very difficult to dissolve (Zong and Xu, 2004). Limestone can also hydrolyze Cd^{2+} to $CdOH^+$, which can be adsorbed tightly by soil, and can thus decrease the availability of Cd (Prasad, 1995). The deposition between Ca^{2+}, Mg^{2+} with Cd^{2+} in Ca-Mg-P fertilizer treatment can also decrease the concentration of available Cd in soil (Prasad, 1995). On the other hand, organic amendments enhance the adsorption of heavy metal by soil through forming stable complexes with heavy metal ions, and then decrease their mobility and extractability (Piccolo, 1996; Naidu *et al*., 1997; Chen, 2000). In this study, the soil pH and the concentrations of available Cu and Cd in the peat treatments were all lower than those in the Ca-Mg-P fertilizer treatments. This may be attributed to the enhanced heavy metal adsorption owing to the large specific surface areas, rich fibre structure, and strong ion exchange capacity introduced by the organic matter in peat treatment (Wang *et al*., 2007).

2.2 Effects of amendments on the growth of rice

All amendments in this study showed some influence on the growth of rice (Table 5). Except for zinc fertilizer, all amendment treatments increased the rice yield and the root biomass. Furthermore, the increase of rice yield and root biomass was significantly consistent with the increasing rates of limestone, silicon fertilizer, pig manure, and peat. At the lower rates of amendments application, rice straw yield was increased by 0.48–4.18 fold, grain yield was increased by 0.3–12.5 fold, and root biomass was increased by 0.68–2.83 fold, respectively, as compared with the control. Table 5 also shows that straw and grain yields

Table 5 Straw and grain yields and root biomass of rice in different treatments

Treatment	Straw yield (g/pot)	Grain yield (g/pot)	Root biomass (g/pot)
Control	10.61 h	1.14 e	1.47 g
L1	54.96 b	15.42 b	5.63 bc
L2	69.27 a	19.91 a	7.73 a
PF1	15.70 gh	1.48 e	2.48 f
PF2	26.82 ef	3.20 e	2.55 f
Si1	21.55 fg	2.46 e	3.21 e
Si2	31.84 de	5.42 d	4.43 d
CMV1	34.85 d	12.06 c	5.46 c
CMV2	36.98 d	12.31 c	5.90 bc
PM1	35.56 d	14.00 bc	5.51 bc
PM2	43.85 c	18.59 a	6.12 b
PE1	22.46 fg	2.68 e	3.32 e
PE2	33.30 de	5.66 d	4.81 d
Zn1	15.56 gh	1.46 e	1.42 g
Zn2	9.89 h	1.41 e	1.41 g

Data are expressed as mean values, and the means with the same small letter in each column are not significantly different at $P < 0.05$.

were enhanced, but root biomass was decreased slightly at the lower rate of zinc fertilizer application. However, the straw yield and root biomass decreased slightly at the higher rate of zinc fertilizer application, despite grain yield being enhanced in the same treatment. Similar result was also reported by Zhu (2003).

Excessive Cu and Cd contents in soil have been reported to restrain the development of root system of plants (Andrei *et al*., 2003), impede photosynthesis (Krupa and Moniak, 1998), and even reduce the crop yield (Verma and Dubey, 2001). The amendments in the present study significantly reduced the bioavailability of Cu and Cd, alleviated their toxicity to rice root, promoted the development of rice root, and therefore enhanced the rice yield (Tables 4 and 5). The rice yield and root biomass at two rates of treatments of different amendments followed the common order: limestone > pig manure > Chinese milk vetch > peat > silicon fertilizer > Ca-Mg-P fertilizer > zinc fertilizer > control, which reversed the order of concentrations of the available Cu and Cd in the soils, except for Chinese milk vetch and peat treatment. The concentrations of available Cu and Cd in peat treatment were lower than those in Chinese milk vetch treatment, but Chinese milk vetch treatment resulted in higher rice yield and root biomass than the peat treatment. This may be related to the lower pH in the peat treatment.

2.3 Effects of amendments on the uptake of Cu and Cd by rice

From Table 6, it is found that the concentrations of Cu ranged from 5.11 to 7.50 mg/kg in grain and from 24.5 to 325 mg/kg in straw in all treatments of amendments application, equivalent to 7.6%–37.0% reduction in grain and 18.8%–93.9% reduction in straw, as compared with the control. The present results also showed that the concentrations of Cd ranged from 0.131 to 0.228 mg/kg in grain and from 0.76 to 2.73 mg/kg in straw, equivalent to 13.8%–50.4% reduction in grain and 31.5%–80.9% reduction in straw, as compared with the control. On the other hand, the concentrations of Cu and Cd in grain and straw of the higher rate treatment were only slightly lower than that of the lower rate treatment of the same amendment, implying that further increase of the application rates may result in little effect on reducing Cu and Cd uptake by rice.

The decrease of Cu and Cd concentrations in grain and straw of rice was related to the change of Cu and Cd fractions in soil. Castaldi *et al*. (2005) found significant decrease of Cd concentrations in root and shoot of white lupin after the addition of compost and lime; they also found that compost and lime decreased the Cd fraction extracted with H_2O and $Ca(NO_3)_2$ and increased the residual fraction of Cd. Narwal and Singh (1998) also reported that pig manure and peat decreased the concentration of DTPA-extractable Cd (available) in soil, but increased Cd in residual fraction. In the present study, the concentrations of available Cu and Cd in the soil of amendments treatments decreased by 3.8%–95.8% and 3.1%–59.7%, respectively (Table 4). Correspondingly, the concentrations of Cu and Cd also decreased by 7.6%–37.0% and 13.8%–50.4% in rice grain, and by 18.8%–93.9% and 31.5%–80.9% in rice straw, respectively, as compared with the control (Table 6). Linear regression analysis revealed significant correlations between the concentrations of available Cu and Cd in soils and the concentrations of Cu and Cd in grain and straw of rice (Eq.(2)). The regression equations (Eq.(2)) are as follows:

Table 6 Concentrations of Cu and Cd in grain and straw of rice in different treatments

Treatment	Cu in grain (mg/kg)	Cd in grain (mg/kg)	Cu in straw (mg/kg)	Cd in straw (mg/kg)
Control	8.12 a	0.264 a	400 a	3.99 a
L1	6.25 bc	0.145 ef	41.4 ef	1.26 cd
L2	5.11 c	0.131 f	24.5 f	1.10 cd
PF1	6.94 ab	0.193 bcde	80.6 de	1.17 cd
PF2	6.82 ab	0.187 bcde	51.7 ef	0.88 d
Si1	6.72 ab	0.165 cdef	226 c	1.59 c
Si2	6.65 ab	0.151 ef	80.8 de	1.34 cd
CMV1	7.50 ab	0.228 ab	51.0 ef	1.06 cd
CMV2	7.42 ab	0.217 abc	38.4 ef	0.76 d
PM1	6.45 bc	0.153 ef	45.6 ef	1.18 cd
PM2	6.24 bc	0.143 ef	26.0 f	0.90 d
PE1	6.62 b	0.156 def	101 d	1.09 cd
PE2	6.41 bc	0.148 ef	65.4 def	0.85 d
Zn1	7.40 ab	0.211 bc	325 b	2.73 b
Zn2	7.14 ab	0.205 bcd	316 b	1.53 c

Data are expressed as mean values, and the means with the same small letter in each column are not significantly different at $P < 0.05$.

For Cu:
$$Y_G = 6.09 + 0.005C_A \ (r = 0.58,\ P < 0.01)$$
$$Y_S = 4.39 + 0.802C_A \ (r = 0.78,\ P < 0.01) \quad (2)$$
For Cd:
$$Y_G = 0.025 + 0.085C_A \ (r = 0.69,\ P < 0.01)$$
$$Y_S = -0.523 + 1.03C_A \ (r = 0.51,\ P < 0.01)$$

where, Y_G and Y_S are the concentrations of Cu and Cd in rice grain and rice straw (mg/kg), respectively. C_A represents the concentrations of available Cu and Cd in soil (mg/kg), respectively. This demonstrates that the bioavailability of Cu and Cd is a key factor controlling the uptake of these metals by rice. Since the concentrations of available Cu and Cd in the soils were significantly affected by the soil pH, significant correlations were also discovered between the soil pH and the concentrations of Cu and Cd in the grain and straw of rice (Eq.(3)), hinting that increasing soil pH may be an effective way in alleviating heavy metals toxicity in the soils. Furthermore, soil adsorption capacity also affected the uptake of heavy metals by plants. For example, organic amendments can increase the absorption and immobilization of these metals in soil, and therefore decrease the uptake of these metals by rice (He and Singh, 1993). Regression equations (Eq.(3)) between the soil pH and the concentrations of Cu and Cd in rice are as follows:

For Cu:
$$Y_G = 11.23 - 0.875\text{pH} \ (r = -0.61,\ P < 0.01)$$
$$Y_S = 738 - 123\text{pH} \ (r = -0.73,\ P < 0.01) \quad (3)$$
For Cd:
$$Y_G = 0.372 - 0.038\text{pH} \ (r = -0.55,\ P < 0.01)$$
$$Y_S = 4.40 - 0.599\text{pH} \ (r = -0.52,\ P < 0.01)$$

where, Y_G and Y_S are the concentrations of Cu and Cd in rice grain and rice straw (mg/kg), respectively.

Table 4 shows that the zinc fertilizer treatment decreased the available Cd concentration by 3.1% for the lower rate and 5.2% for the higher rate. However, Cd concentrations decreased by 20.2% and 22.5% in rice grain and by 31.5% and 61.6% in rice straw, respectively (Table 6), a significant greater decrease than that of the available Cd in the soils. This was because of the competition between Zn^{2+} and Cd^{2+}, either externally at the root surface or within the plant (Lauchli and Bieleski, 1983). In addition, the decrease of Cu and Cd concentrations in grain and straw of rice in the treatments of amendments application may be partially attributed to the dilution effect caused by the significant increase of rice yield.

Copper concentration in rice straw at two rates of treatments of different amendments followed the same order: limestone < pig manure < Chinese milk vetch < Ca-Mg-P fertilizer < peat < silicon fertilizer < zinc fertilizer < control, while that of Cd followed the order: Chinese milk vetch < peat < Ca-Mg-P fertilizer < pig manure < limestone < silicon fertilizer < zinc fertilizer < control. The concentrations of Cu and Cd in rice grain were lower than those in straw regardless of the rates or sources of amendments (Table 6); they followed the order: limestone < pig manure < peat < silicon fertilizer < Ca-Mg-P fertilizer < zinc fertilizer < Chinese milk vetch < control. The concentrations of Cu and Cd in grain in Chinese milk vetch treatment were higher than in any other amendments treatment, whereas the concentrations in rice straw in Chinese milk vetch treatment were lower than in most other amendments treatments. This was probably attributed to the difference in transferring Cu and Cd from rice straw to grain. Wang *et al*. (1999) reported that Chinese milk vetch promoted the transfer of Cu from rice straw to grain in red soil.

Although the soil in this study was seriously contaminated by Cu and Cd, Cu concentrations in grain still did not exceed the tolerance limit of copper (10 mg/kg) in foods (MHC, 1994). After the application of limestone, Ca-Mg-P fertilizer, silicon fertilizer, pig manure, and peat, the Cd concentrations in grain were all below the tolerance limit of cadmium (0.2 mg/kg) in foods (MHC, 1994), whereas the Cd concentrations in grain in zinc fertilizer, Chinese milk vetch treatments, and the control exceeded the limit by 2.5%–32.0%. The high Cd concentration in grain for zinc fertilizer treatment implied that zinc sulfate may not be suitable for the ameliorateion of the soil; the excess of Cd concentration in grain in Chinese milk vetch treatment suggested that Chinese milk vetch should be avoided to use for the soil remediation. The present results indicated that limestone, Ca-Mg-P fertilizer, silicon fertilizer, pig manure, and peat significantly enhanced the yield of rice and decreased the concentrations of Cu and Cd in rice straw and grain. Field investigations must be done to understand the long-term effects of their application on rice growth.

3 Conclusions

Application of amendments induced rice growth, and significantly increased the yield of rice grain and rice straw as well as the rice root biomass. Soil pH was increased and the bioavailability of Cu and Cd was decreased significantly consistent with increasing rates of amendments application. Limestone demonstrated the best efficiency among all the amendments in this study; it increased grain yield by 12.5–16.5 fold and decreased the concentrations of Cu and Cd in rice grain by 23.0%–50.4%. Application of Ca-Mg-P fertilizer, silicon fertilizer, pig manure, and peat also increased the grain yield by 0.3–15.3 fold, yet reduced the Cu and Cd concentrations in rice grain below the tolerance limits of Cu and Cd in foods. However, Cd concentrations in rice grain in Chinese milk vetch and zinc fertilizer treatments exceeded the limit by 2.5%–14.0%. The concentrations of Cu and Cd in rice grain and rice straw were significantly correlated to the concentrations of available Cu and Cd in the soils. The soil available Cu and Cd were significantly affected by the soil pH, and the soil adsorption capacity also affected the bioavailability of Cu and Cd in the soils. Therefore, both soil pH and available heavy metal are important in predicting the metal concentrations in plants. Based on these results, limestone at the rate of 1500–4500 kg/hm^2 should be recommended to remediate the contaminated soil.

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