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RESEARCH ARTICLE

Si-Ca-K-Mg amendment reduces the phytoavailability and transfer of Cd from acidic soil to rice grain

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Abstract

Cadmium (Cd) contamination in the soil-rice chain is the major threat to human health in China. It is very necessary to lower Cd phytoavailability in contaminated soils and reduce Cd transfer from soil to rice for food safety. This study applied the Si-Ca-K-Mg amendment (SCKM) to immobilize Cd in acidic soils and then reduce its accumulation in rice grain (Oryza sativa L.). Two agricultural soils (Alfisol and Ultisol) collected from Eastern China were treated with three levels of Cd concentration (0, 0.4, and 2.0 mg/kg), respectively, for pot experiment. The phytoavailability and chemical forms of Cd in two soils were determined using ethylenediaminetetraacetic acid (EDTA) and the European Community Bureau of Reference (BCR) extraction procedures. At 2.0 mg Cd/kg-treated soils, application of SCKM amendment increased the yield of rice grain by 10–17% for Alfisol and 14–39% for Ultisol, and reduced the concentrations of EDTA-extractable Cd by 6–27% for Alfisol and 5–25% for Ultisol, compared with treatment without amendment. SCKM amendment significantly ($p < 0.05$) reduced the bioconcentration factor (BCF) of Cd in root, straw, and grain of rice. Compared with treatment without amendment, the application of amendments decreased the Cd concentrations of rice grains by 35–76% for Alfisol and 31–72% for Ultisol, respectively. The BCR sequential extraction revealed that amendment reduced acid soluble Cd fraction by 6.2–13.6% for Alfisol and 6.1–13.5% for Ultisol, respectively, indicating that amendment could effectively transform the highly phytoavailable Cd into a more stable form. SCKM amendment addition significantly ($p < 0.05$) increased soil pH and exchangeable K^+, and decreased exchangeable Al^{3+} contents in both soils. Our results demonstrated that SCKM amendment was effective in reducing the phytoavailability and transfer of Cd in soil-rice system, and ameliorating soil acidity. The SCKM amendment had greater potential as a low-cost and friendly environmentally amendment for safe production of rice in Cd-contaminated soils.

Keywords Cadmium (Cd) · Rice · EDTA · SCKM amendment · Acid soils

Introduction

Cadmium (Cd) contamination of agricultural soils is one of the most significant environmental issues in China. A recent national-scale survey indicated that about 7% of Chinese soils had been polluted by Cd (Ministry of Environmental Protection of PRC 2014). Most of Cd-contaminated soils, mainly distributed in southern and eastern parts of China, are used for rice plantation. Rice is one of the most important food crop in China. However, the rice plant readily takes up the Cd of soil and translocate the Cd into the rice tissues, which lead to higher Cd accumulation of rice grain even the concentration of Cd the soil is quite low (Liu et al. 2007; Meng et al. 2018). The Cd concentration of over 10% of brown rice collected from China's rice market exceeded the national food standard for brown rice Cd (0.2 mg/kg) (Li and Xu 2015). Wang et al. (2016) reported that the Cd

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concentrations of more than 70% rice grains collected in the acidic paddy soil of Hunan, China, exceeded the maximum permissible concentration of Cd according to the National Food Safety Standard of China (GB 2762-2017). In addition, soil acidification was greatly enhanced in recent decades due to application of a large of chemical fertilizers (Guo et al. 2010). Soil acidification can greatly enhance the mobility and phytoavailability of Cd in soils, and consequently increase the risk of Cd contamination in rice. Thus, Cd toxicity of rice has been identified as the major threat to human health through the soil-rice food chain. Because of the great public concern regarding minimizing intake of Cd from rice, there is an urgent need to develop efficient soil amendments to reduce Cd phytoavailability in soils and potential risk of Cd contamination in rice.

In recent years, a number of amendments to eliminate Cd contamination in soil-rice system have been applied, such as lime, alkaline materials, organic amendments, and phosphate (Bian et al. 2014, 2016; Inkham et al. 2019; Juang et al. 2012; Meng et al. 2019; Zhou et al. 2014). Laboratory and field experiments demonstrated that application of lime, phosphate fertilizer, and biochars significantly decreased the Cd content of rice grain. In acidic soils, the application of lime and alkaline materials generally showed better inhibitory effects on the availability of Cd (Hamid et al. 2019; Inkham et al. 2019; Nie et al. 2019). Among these amendments, alkaline material or fertilizers can offer pronounced economic and environmental benefits. Lime has proven as the most suitable amendment for reducing the Cd toxicity and soil acidity in acidic soils. A combination of low-Cd-accumulation rice cultivar and in situ immobilization with soil amendment is an effective approach for safe rice production in Cd-contaminated paddy soils (Meng et al. 2018, 2019). However, these amendments do not supply the necessary mineral nutrients for rice growth. More importantly, the long-term application of lime would lead to lower soil fertility. Therefore, it is the key to develop a cheap and broad benefits amendment to remediate soil acidity, increase soil fertility, and reduce the Cd toxicity in rice in Cd-contaminated soils.

Higher Cd mobility in the acidic soils suggests that acidity control and in situ immobilization of Cd should be implemented simultaneously in the acidified Cd contaminated soils. In order to remedy Cd-contaminated soils and produce safe food, there is a great need for developing a range of cost-effective and environmentally soil amendments. Therefore, it is preferentially required to develop the multifunctional amendment with alkaline nature and Cd immobilization to reduce the accumulation of Cd in rice grains and remedy soil acidity. In this study, a new amendment of reducing Cd phytoavailability and soil acidity, and providing mineral nutrients for rice plant was tested by using a pot experiment. The purposes of this study were (1) to assess the potential of Si-Ca-K-Mg amendment (SCKM) on reducing Cd phytoavailability and remedying soil acidity, (2) to explore the possible mechanisms of amendment in reducing Cd phytoavailability and transfer in soil-rice system, and (3) to illustrate the potential of SCKM as a low-cost and friendly environmentally amendment in safe rice production.

Materials and methods

Soils and amendment

Two soils, paddy soil (Alfisol) and red soil (Ultisol), were collected from the topsoil layer (0–20 cm in depth) of typical agricultural lands in Quzhou and Dongyang city, Eastern China. Soil samples were air-dried at room temperature, ground, and then passed through a 2-mm sieve. The physicochemical properties of two studied soils are shown in Table 1. Each soil sample was respectively spiked with two concentrations of Cd (0.4 and 2.0 mg/kg) in the form of $CdSO_4 \cdot 8/3H_2O$ solution. The added Cd concentrations were based on the Soil Environmental Quality-Risk Control Standard for Soil Contamination of Agricultural Land (GB15618-2018) (Ministry of Ecology and Environment of the People's Republic of China 2018). The Cd concentrations of 0.4 and 2.0 mg/kg were defined as risk screening value and risk intervention value for soil contamination of agricultural land, respectively. The initial concentrations of Cd in Alfisol and Ultisol were 0.24 and 0.26 mg/kg, respectively. The Cd-spiked soils were aged for 90 days at 80% field water capacity. Then, each Cd-spiked soil samples was air-dried again, and ground to pass through a 2-mm sieve for the pot experiment. The Si-Ca-K-Mg amendment (SCKM) was alkaline fertilizer calcined by phosphogypsum and potassium feldspar at high temperature (1000–1100°C). It contains > 25% SiO_2, 25% CaO, > 5% MgO, > 8% K_2O, and small amount of microelements. The Cd content of amendment was 0.08 mg/kg.

Table 1 Physicochemical properties of soils used in pot experiment

Soil properties	Unit	Ultisol	Alfisol
pH		5.87	5.80
Soil organic matter (SOM)	g/kg	25.30	23.53
Sand(2000–20 μm)	g/kg	418.8	587.7
Silt(20–2 μm)	g/kg	401.3	272.3
Clay(< 2 μm)	g/kg	179.9	140.0
Cation exchange capacity (CEC)	cmol/kg	13.58	8.33
Total P	g/kg	4.58	6.42
Total N	g/kg	0.22	0.32
Total K	g/kg	30.28	47.60
Total Cd	mg/kg	0.26	0.24

Pot experiment

Each Cd-treated soil was transformed into three plastic pots (5 kg soil each pot). Soil amendments at the rate of 0, 0.1, and 0.2% were added into the pot and homogenously mixed. The treatments were numbered as T0, T1, and T2, respectively. Soils treated without the Cd were taken as the control treatment (CK). Three replicates of each treatment were performed. Each pot was added with 0.15 g N/kg of urea, 0.05 g P/kg of KH_2PO_4, and 0.1 g K/kg of K_2SO_4 as basal fertilizer. The pot incubation experiment was conducted in a greenhouse. The rice cultivar (Zhongzheyou 8) was selected as the trial crop. Three seedlings of rice were transplanted to each pot. The pot maintained a 2-cm layer of water during the growing period of rice plant.

Plant analysis

After maturity, the rice plant was harvested and separated into three parts: root, straw (stem and leaves), and grain. The plant tissues were washed several times with deionized water, and oven dried at 80 °C. Total dry weight of the rice grain was measured. These tissues were then ground to pass through a 100-mesh nylon sieve for analysis of Cd element. The rice tissue samples were digested using a mixture solution of nitric acid, hydrofluoric acid, and hydrogen peroxide (5:1:2 in volume ratio) in microwave oven (MASTER 40, SINEO, China) (Bao 2008). The digestion solution was then diluted to 10 mL with ultra-pure water. The concentrations of Cd in the solution were analyzed using an inductively coupled plasma mass spectroscopy (ICP-MS, PerkinElmer NexIONTM 300X, USA).

Soil chemical analysis

After rice harvest, the soil samples of pot experiment were collected and air-dried at room temperature. The soil samples were than ground to pass a 100-mesh sieve for chemical analyses. Soil pH was determined in 1:2.5 soil/water suspensions using pH meter (PB-21, Sartorius). Soil exchangeable acidity was extracted with 1 M KCl and determined by titration with 0.02 M NaOH (Bao 2008). Soil exchangeable cations were extracted with 1.0 M ammonium acetate method. Exchangeable Ca^{2+} and Mg^{2+} were determined by atomic absorption spectrophotometer and exchangeable K^+ and Na^+ by flame photometer (Bao 2008). The soils were digested by using concentrated nitric acid, hydrofluoric acid, and hydrochloric acid (5:2:2 in volume). The total Cd was determined with an inductively coupled plasma mass spectroscopy (ICP-MS, PerkinElmer NexIONTM 300X, USA). Quality control included reagent blanks, replicate samples, and standard reference materials.

An estimation of the phytoavailable fraction of Cd in the soils was determined using ethylenediaminetetraacetic acid (EDTA) extraction technique (Rodrigues et al. 2013). Briefly, 1 g of soil was extracted with 20 mL of 0.05 M EDTA solution in a centrifuge tube. The centrifuge tube was agitated on an end-over-end shaker for 2 h after which it was centrifuged at 3500 rpm for 10 min. After filtering, the concentrations of Cd in the extract solution were determined by ICP-MS. The chemical forms of Cd in soils were analyzed by the European Community Bureau of Reference (BCR) procedure (Ahnstrom and Parker 1999; Quevauviller et al. 1993). The BCR technique operationally separates Cd into four different chemical forms: extractable with 0.11 M HAc (acid-soluble, Fi), extractable with 0.05 M $NH_2OH{\cdot}HCl$ (pH = 1.5) (reducible, Fii), extractable with 30% H_2O_2 + 1 M NH_4OAc (pH = 2.0) (oxidizable, Fiii), and HNO_3-HF-HCl digested (residual, Fiv). After each extraction, the solution was separated from the solid phase by centrifuging at 3500 rpm for 30 min, and then filtered through 0.45-μm filter paper. The residue was washed with ultrapure water and then used for the subsequent step. The Cd concentration in extract solution was analyzed using ICP-MS.

Bioconcentration and translocation factors of Cd for the rice plants

The bioconcentration factor (BCF) of Cd was defined as the ratio of Cd concentration of rice tissues (Cd_{rice}) at harvest to the Cd concentration in soils (Cd_{soil}):

$$BCF = Cd_{rice}/Cd_{soil}$$

The translocation factor (TF) of Cd is defined as the ratio of the Cd concentration in rice straw and grain ($Cd_{straw\ or\ grain}$) to those in rice roots and straw ($Cd_{root\ or\ straw}$):

$$TF = Cd_{straw\ or\ grain}/Cd_{root\ or\ straw}$$

The TF value shows the tendency of Cd to move toward the aerial tissues of rice plants from the rice roots. At a TF < 1, Cd is immobilized in the root of rice; otherwise, Cd is enriched more in the straw than in the root of rice.

Statistical analysis

All data in figures and tables are shown as means ± SD of three replicates. A one-way analysis of variance (ANOVA) was used for statistical analysis, followed by the LSD test to determine the significant difference ($p < 0.05$) between the means of different treatments. All statistical analyses were performed using the SPSS 20.0, and all figures were drawn using Origin 9.0 software.

Results

Rice grain yield

The effects of SCKM amendments on rice grain yield are shown in Fig. 1. The increased levels of Cd in soils decreased the rice grain yield, but the differences were not significant comparing the control treatment (CK). The Cd-contaminated Alfisol exhibited larger reduction in the yield of rice grain than Ultisol compared with the control treatment (CK). The application of amendments to soil significantly increased the yield of rice grain. At 0.4 mg Cd/kg-treated soils, the T1 and T2 treatment increased the yield of rice grain by 17–27% for Alfisol and 14–29% for Ultisol, respectively, compared to the treatment without amendment (T0). At 2.0 mg Cd/kg-treated soils, the T1 and T2 treatments increased the yield of rice grain by 10–17% for Alfisol and 14–39% for Ultisol, respectively. The pot experimental results demonstrated that the effect of SCKM amendment on the growth of rice plants was more pronounced in Ultisol than in Alfisol.

Cd concentrations in rice tissues

The effects of SCKM amendments on Cd concentrations of root, straw, and grain in rice crop are shown in Fig. 2 and Table S1. The increased Cd concentration in soil largely increased the Cd concentration of rice grain. At 2.0 mg Cd/kg-treated soils, the Cd concentration of rice grain was as high as 4.38 and 4.18 mg/kg for Alfisol and Ultisol, respectively, which largely exceed the maximum permissible concentration for Cd in brown rice in China. SCKM amendment significantly ($p < 0.05$) reduced the Cd concentration of rice grain (Fig. 2). At 2.0 mg Cd/kg-treated Alfisol, the application of SCKM amendment at the rate of 0.1 and 0.2% significantly decreased the Cd concentrations of rice grains by 49% and 76%, respectively, compared to the treatment without amendment (T0). Similar results were observed in Ultisol.

The Cd concentrations in three tissues of rice crop increased in the following order: root> > straw>grain (Table S1). The Cd concentrations of root and straw significantly ($p < 0.05$) increased with increasing the Cd levels in two soils. The Cd-contaminated soils resulted in significant increase of Cd concentrations in root and straw tissues of rice crop. The concentration of Cd in rice root grown on Ultisol was approximately 10 times more than that in rice grain. The root and straw tissues of rice showed strong capacity to retain Cd rather than transport Cd to the grain. The higher accumulation of Cd in root and straw of rice indicated that a higher proportion of the Cd taken up by rice remained in the root, leave, and stem of rice plant. Compared with the control, the 0.1 and 0.2% SCKM amendment resulted in significant reduction of Cd concentration in rice root. Similarly, the concentration of Cd in rice straw significantly ($p < 0.05$) decreased with addition of amendment (Table S1). Therefore, application of SCKM amendment was efficient in reducing Cd uptake by rice tissues.

Accumulation and translocation of Cd in soil-rice system

Table 2 lists bioconcentration factor (BCF) and translocation factor (TF) for rice plant grown in Cd-contaminated soils. At the control treatment (CK), BCF values of rice grain in two soils were 0.80. Moreover, BCF values of rice root and straw in Alfisol were much lower than those in Ultisol. The BCF values of root and straw were much larger than that of rice grain, indicating that the root and straw of rice is major accumulator of Cd. The application of SCKM amendment to Cd-contaminated soils significantly ($p < 0.05$) reduced the accumulation of Cd in rice plant tissues, indicating that they could restrain the uptake of Cd by rice plant. At 2.0 mg Cd/kg-

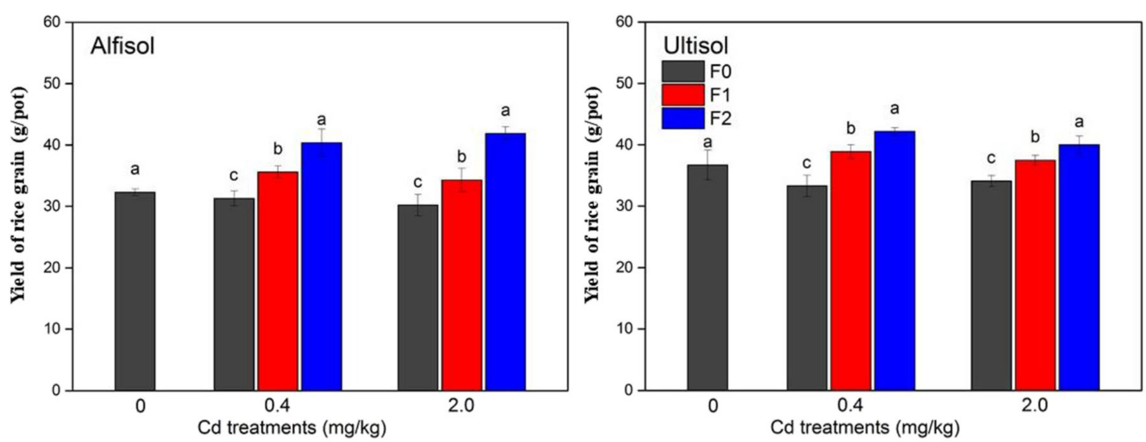

Fig. 1 Effect of Si-Ca-K-Mg amendment (SCKM) on rice grain yield of both soils. The different letters (a, b, c) indicate significant differences ($p < 0.05$) between SCKM treatments. The T0, T1, and T2 were the application rate of SCKM amendment at the rate of 0, 0.1, and 0.2%, respectively

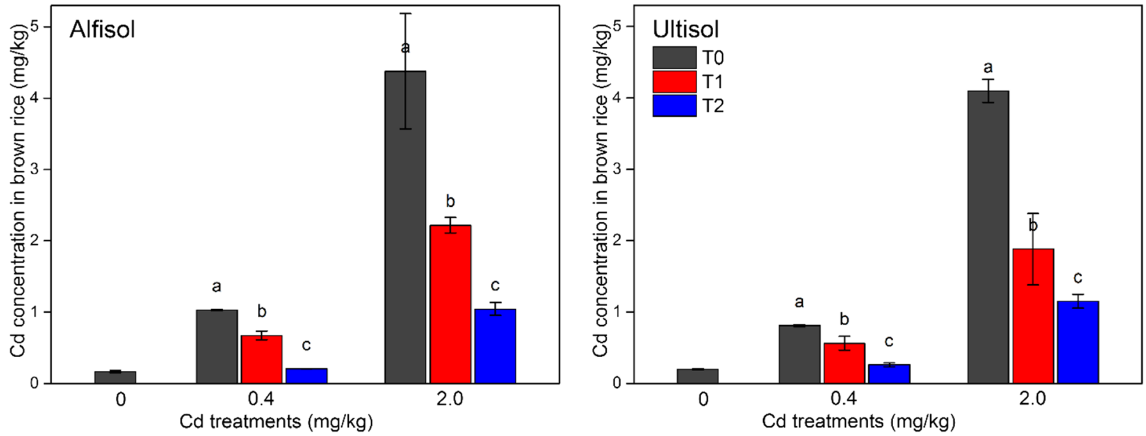

Fig. 2 Effect of Si-Ca-K-Mg amendment application on Cd concentration in rice grain. The different letters (a, b, c) indicate significant differences ($p < 0.05$) between SCMP treatments

treated Alfisol, the application of SCKM amendment decreased the BCF of rice root from 13.4 in the treatment (T0) to 6.8 and 3.5 in the T1 and T2 treatments, respectively. Similarly, SCKM amendment reduced the BCF of rice root in Ultisol from 13.4 to 7.0 and 4.5, respectively.

The translocation factor (TF) is widely used to assess the transfer capacity of heavy metals from the soil to plant, or from one part of the plant to another. Generally, the SCKM amendments decreased the TF value of Cd from root to straw in rice crop, implying that the amendments could restrain the transfer of Cd from rice root to straw tissue. At 2.0 mg Cd/kg-treated soils, the TF value of Cd in T2 treatment was significantly lower than the T0 treatment. The average TF value of Cd decreased by 25.0% for Alfisol and 14.7% for Ultisol, respectively. The TF value of straw to grain in rice stands for translocation tendency of Cd to move toward the grain of rice from the stem and leave tissues of rice. The TF value from rice straw to grain was less than one, indicating that Cd is immobilized in the stem and leave tissues of rice. However, the effects of SCKM amendment on TF value of Cd from straw to grain were not significant compared with T0 treatment. In addition, the TF values of Cd from straw to grain in Alfisol were much larger than those in Ultisol. The decreased TF values of Cd from root to stem and leave, particularly for high dosage application, indicated that applied amendment decreased Cd transport from root to stem and leave of rice.

Table 2 Bioconcentration factor (BCF) and translocation factor (TF) for rice plants.

Treatments	BCF			TF	
	Root	Straw	Grain	Root-straw	Straw-grain
Alfisol					
CK	8.8 ± 3.4	1.9 ± 0.8	0.8 ± 0.3	0.22 ± 0.01	0.41 ± 0.01
Cd0.4 T0	13.2 ± 6.3a	3.9 ± 1.2a	1.9 ± 0.9a	0.31 ± 0.05a	0.47 ± 0.08a
Cd0.4 T1	7.6 ± 0.7a	2.1 ± 0.0b	1.1 ± 0.1ab	0.28 ± 0.02a	0.50 ± 0.04a
Cd0.4 T2	2.6 ± 1.2b	0.7 ± 0.2c	0.4 ± 0.2b	0.28 ± 0.06a	0.52 ± 0.11a
Cd2.0 T0	11.2 ± 0.9a	3.1 ± 0.1a	1.9 ± 0.1a	0.28 ± 0.03a	0.63 ± 0.04a
Cd2.0 T1	6.8 ± 0.8b	1.6 ± 0.1b	1.1 ± 0.2b	0.24 ± 0.04ab	0.67 ± 0.14a
Cd2.0 T2	3.5 ± 0.2c	0.7 ± 0.0c	0.5 ± 0.1c	0.21 ± 0.02b	0.71 ± 0.11a
Ultisol					
CK	22.2 ± 6.5	4.6 ± 1.3	0.8 ± 0.2	0.21 ± 0.01	0.17 ± 0.01
Cd0.4 T0	16.2 ± 3.0a	6.3 ± 1.1a	1.2 ± 0.2a	0.39 ± 0.01a	0.19 ± 0.01c
Cd0.4 T1	12.5 ± 0.8b	3.7 ± 0.6b	0.8 ± 0.1b	0.30 ± 0.03b	0.22 ± 0.01b
Cd0.4 T2	6.4 ± 0.1c	1.6 ± 0.1c	0.4 ± 0.0c	0.25 ± 0.01c	0.24 ± 0.01a
Cd2.0 T0	13.4 ± 2.3a	4.6 ± 0.7a	1.8 ± 0.3a	0.34 ± 0.01a	0.39 ± 0.02a
Cd2.0 T1	7.0 ± 1.6b	2.4 ± 0.4b	0.8 ± 0.1b	0.35 ± 0.03a	0.33 ± 0.01b
Cd2.0 T2	4.5 ± 0.3b	1.3 ± 0.1c	0.5 ± 0.0b	0.29 ± 0.01b	0.38 ± 0.02a

All values are presented as mean ± SD ($n = 3$)

The different letters in the same column indicate significant differences between SCMP treatments ($p < 0.05$)

Total Cd and EDTA-extractable Cd concentrations in the soil

The total and EDTA-extractable Cd concentrations in soils are shown in Fig. 3. No significant changes in total Cd were observed after SCKM amendment was added into two soils. Available metals refer to the fraction of metals that can be directly uptaken by plants (Adriano 2001). In our study, EDTA-extractable Cd was used to stand for phytoavailabile Cd in soils. The concentrations of EDTA-extractable Cd in soils amended with SCKM amendment were lower than those in the control treatment. This reduction of EDTA-extractable Cd concentration was increased with increasing addition rate of amendment. The EDTA-extractable Cd in the soil decreased drastically when the addition amount of amendment increased from 0 to 0.2%. At 2.0 mg Cd/kg-treated Alfisol, the concentration of EDTA-extractable Cd decreased from 1.45 mg/kg in treatment (T0) to 1.01 mg/kg in T2 treatment. In Ultisol, it decreased from 1.65 to 1.24 mg/kg. Linear regression analysis indicated highly significant correlation between the EDTA-extractable Cd concentrations in soils and the Cd concentrations of rice grains (r = 0.837, p < 0.01).

Chemical forms of Cd in the soil

Distributions of various chemical forms of Cd in soils are described in Fig. 4. Concentrations of Cd in Ultisol were in the decreasing order of acid-soluble fraction (Fi) ≈ residual fraction (Fiv) > reducible fraction (Fii) >, and oxidizable fraction (Fiii), while Alfisol in the form of Fiv > F(i) > F(ii) > F(iii) fractions. Results showed that Cd in Cd-treated soils was predominantly existed in the acid soluble form (Fi). The Fi fraction of Cd in contaminated soils accounted for 44–59% of total Cd in two soils. For the control soils without Cd treatment, acid-soluble fractions of Alfisol and Ultisol were about 29% and 34%, respectively. The concentrations of various chemical forms of Cd in two soils increased as the level of spiked Cd (Table S1), indicating that the added Cd redistributed between the various chemical forms. Application of amendment at the rate of 0.1 and 0.2% into two soils significantly (p < 0.05) decreased the concentration of acid-soluble form (Fi), but significantly increased the concentration of residual (Fiv) form. In the 0.4 and 2.0 mg Cd/kg-treated Ultisol, the acid soluble Cd fraction in soil was reduced by 10% and 13%, while the residual Cd fraction was increased by 6% and 12%, respectively. However, no significant

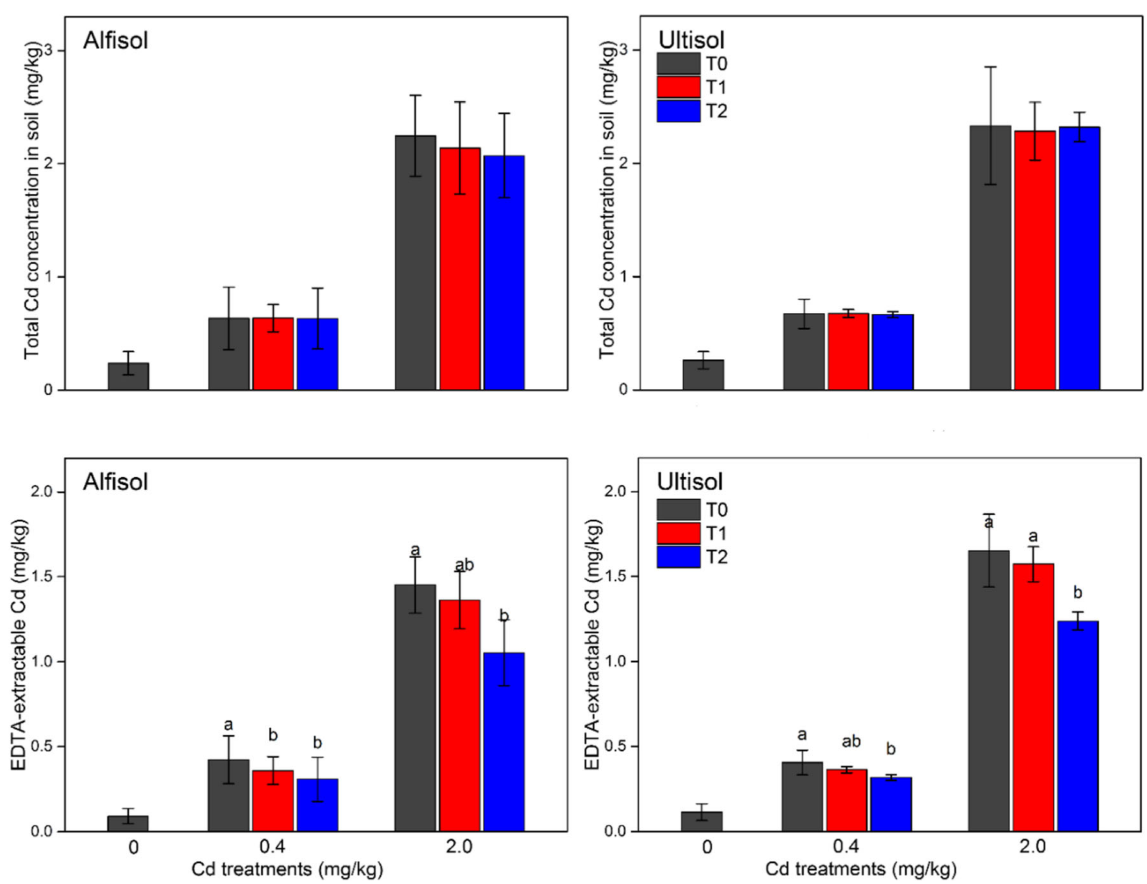

Fig. 3 Effect of Si-Ca-K-Mg amendment application on total and EDTA-extractable Cd concentrations in soils. The different letters (a, b, c) indicate significant differences (p < 0.05) between SCMP treatments

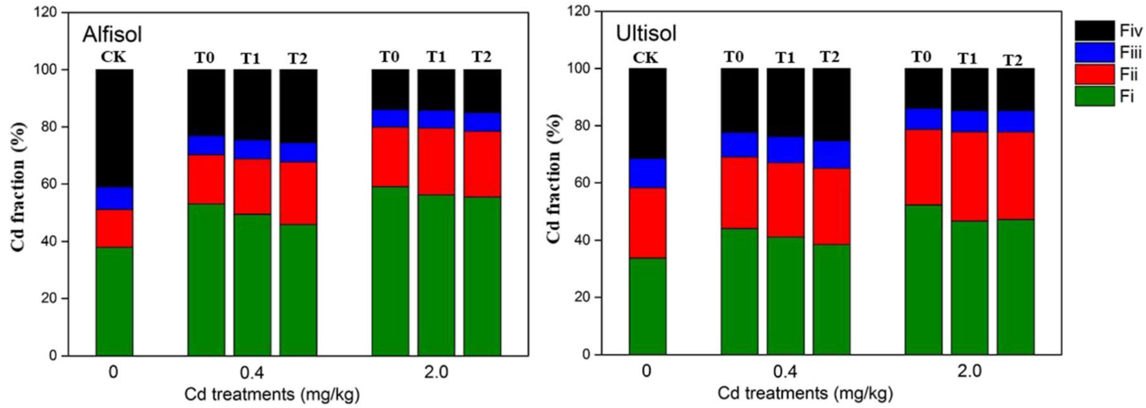

Fig. 4 Effect of Si-Ca-K-Mg amendment application on the percentage of Cd chemical forms in soils. Fi, acid soluble fraction; Fii, reducible fraction; Fiii, oxidizable fraction; Fiv, residual fraction

changes in reducible and oxidizable forms in Cd-treated soils were found. The sequential extraction results (Fig. 4) demonstrated that SCKM amendment shifted Cd chemical forms from phytoavailable to less phytoavailable forms, indicating that SCKM amendments could reduce the phytoavailability of Cd by changing the distribution of Cd chemical forms in soils. Consequently, the transformation of Cd chemical forms reduced the transfer of Cd from soil to rice crop.

Soil pH and exchangeable cations

Soil acidification commonly increases the mobility and availability of toxic metals in soils, resulting in increased plant uptake and subsequent transfer in soil-crop food chain. Application of SCKM amendment increased soil pH (Fig. 5). Soil pH increased with increasing the addition amount of SCKM amendment. The 0.2% amendment significantly ($p < 0.05$) increased the pH of two soils, which increased by 0.60 and 0.73 units for Ultisol and Alfisol treated with 2.0 mg Cd/kg, respectively, compared with the control (T0). Application of SCKM amendments significantly decreased exchangeable Al^{3+} and H^+ concentrations and increased K^+ concentrations in soil (Table 3). In Alfisol, exchangeable Al^{3+} concentrations of T1 and T2 treatments were lower 14% and 18% for soils treated with 0.4 mg Cd/kg and 16% and 19% for soils treated with 2.0 mg Cd/kg, respectively. In Ultisol, they were 19% and 40% as well as 18% and 38%, respectively. The SCKM amendment significantly increased exchangeable Ca^{2+} concentrations in Alfisol, but no significant difference was found in Ultisol.

Relationships between Cd concentrations of various chemical forms and rice grain

Table 4 shows the correlation coefficients between Cd concentrations of various chemical forms in soils and rice grain. The Cd concentrations of rice grain were positively correlated with the acid-soluble Cd concentrations in soils ($r = 0.704$, $p < 0.01$), but negatively correlated with residual fraction ($r = -0.690$, $p < 0.01$). However, the reducible and oxidizable Cd were not significantly correlated with rice Cd concentration. In this experiment, the concentrations of acid-soluble Cd in soils had strong negative correlation with soil pH. The results also indicated that acid-soluble Cd concentration was highly correlated with EDTA-extractable Cd concentration ($r =$

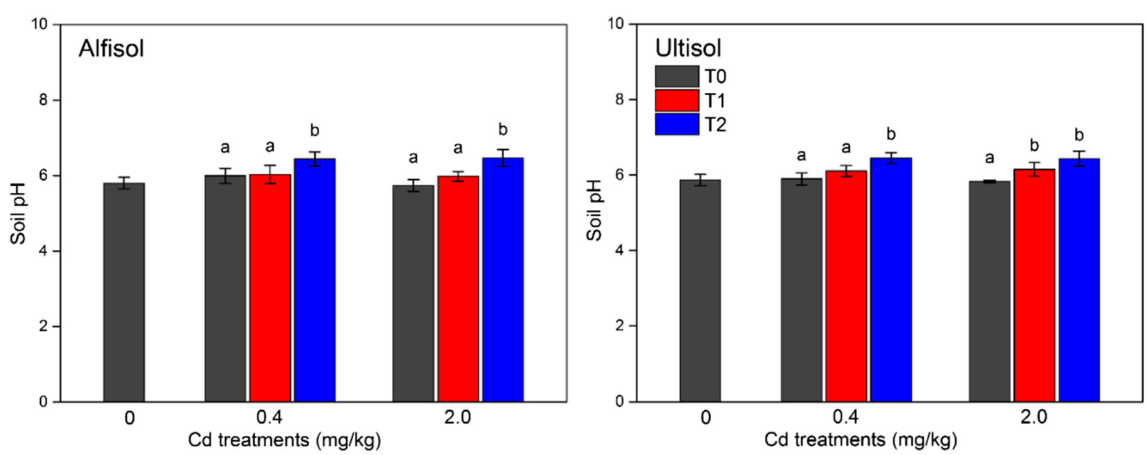

Fig. 5 Effect of Si-Ca-K-Mg amendment application on soil pH. The different letters (a, b, c) indicate significant differences ($p < 0.05$) between SCMP treatments

Table 3 Effects of SCKM amendment on exchangeable H^+, Al^{3+}, and exchangeable cation content in two soils.

Treatments	Exchangeable acid (cmol/kg)		Exchangeable base ions (cmol/kg)			
	Al^{3+}	H^+	K^+	Na^+	Ca^{2+}	Mg^{2+}
Alfisol						
CK	2.49 ± 0.04a	0.50 ± 0.04a	0.55 ± 0.02a	0.55 ± 0.06a	3.09 ± 0.27a	1.15 ± 0.01a
Cd0.4 T0	2.44 ± 0.08a	0.55 ± 0.02a	0.57 ± 0.01a	0.67 ± 0.05b	3.35 ± 0.07b	1.15 ± 0.02a
Cd0.4 T1	2.10 ± 0.02b	0.52 ± 0.03ab	0.56 ± 0.27a	1.26 ± 0.07a	3.32 ± 0.04b	1.14 ± 0.04a
Cd0.4 T2	2.00 ± 0.03b	0.49 ± 0.03b	0.60 ± 0.01a	0.30 ± 0.01c	4.33 ± 0.56a	1.08 ± 0.02b
Cd2.0 T0	2.45 ± 0.04a	0.55 ± 0.03a	0.51 ± 0.01b	0.47 ± 0.01b	3.36 ± 0.02b	1.15 ± 0.01b
Cd2.0 T1	2.04 ± 0.02b	0.55 ± 0.02a	0.51 ± 0.03b	0.58 ± 0.01a	3.62 ± 0.06b	1.21 ± 0.04a
Cd2.0 T2	1.96 ± 0.03c	0.52 ± 0.04a	0.56 ± 0.01a	0.45 ± 0.01c	4.48 ± 0.55a	0.97 ± 0.01c
Ultisol						
CK	4.98 ± 0.03a	1.49 ± 0.03a	0.61 ± 0.01a	0.27 ± 0.02a	1.63 ± 0.01a	0.22 ± 0.01a
Cd0.4 T0	4.95 ± 0.03a	1.48 ± 0.03a	0.63 ± 0.02c	0.17 ± 0.05a	1.70 ± 0.24a	0.23 ± 0.01c
Cd0.4 T1	4.00 ± 0.06b	1.00 ± 0.03b	0.74 ± 0.01b	0.15 ± 0.01a	1.75 ± 0.10a	0.24 ± 0.01b
Cd0.4 T2	2.99 ± 0.08c	1.00 ± 0.04b	0.96 ± 0.01a	0.09 ± 0.01b	1.87 ± 0.04a	0.25 ± 0.01a
Cd2.0 T0	4.90 ± 0.02a	1.60 ± 0.04a	0.63 ± 0.02c	0.14 ± 0.01b	1.52 ± 0.04a	0.22 ± 0.01a
Cd2.0 T1	4.00 ± 0.06b	0.97 ± 0.03c	0.74 ± 0.01b	0.38 ± 0.03a	1.54 ± 0.26a	0.18 ± 0.01c
Cd2.0 T2	3.05 ± 0.07c	1.04 ± 0.03b	0.85 ± 0.01a	0.32 ± 0.05a	1.69 ± 0.14a	0.20 ± 0.01b

The different letters in the same column indicate significant differences between SCKM treatments ($p < 0.05$)

0.698, $p < 0.01$). Highly significant relationships were observed for both rice tissues and EDTA-extractable Cd. This indicated that the acid-soluble Cd and EDTA-extractable Cd gave enough information to predict the phytoavailability of Cd in soils and accumulation of Cd in rice. Therefore, this close correlation demonstrated that acid-soluble form and EDTA-extractable Cd was the major pool for Cd uptake of rice crop.

Discussion

In this study, it was found that the SCKM amendment could effectively reduce Cd phytoavailability in soils and its transfer from soil to rice tissues, particularly in rice grain. The possible mechanisms involved in amendment effects could be associated with several processes. Firstly, the increased pH induced by adding SCKM amendment resulted in reducing phytoavailable Cd concentration in soils. The reduction in phytoavailable Cd concentration in the soil decreased the uptake of Cd into root of rice plant. In acidic soils, H^+ ion has a higher binding capacity to soil particles than other cations, which could replace other cations on the surface of soil colloids. Therefore, lower soil pH could increase the competition between H^+ ion and Cd ion bound with soil particles, resulting in release of Cd into soil solution. The replacement of Cd by H^+ ion enhances the phytoavailability of Cd in soils. As application of SCKM amendment enhanced soil pH, Cd ion tended to bind with free hydroxyl groups in soil solution. The formation of hydrous Cd oxides would decrease the phytoavailability of Cd. In addition, the increased soil pH could also form Cd precipitate like carbonates, sulfates,

Table 4 Correlation coefficients between the concentrations and chemical forms of Cd in soils and Cd concentration of rice grain

	Cd_{rice}	Total Cd	EDTA-Cd	Fi	Fii	Fiii	Fiv
Cd_{rice}	1	0.760^{**}	0.837^{**}	0.704^{**}	0.170	− 0.487	-0.690^{**}
Total Cd		1	0.980^{**}	0.702^{**}	0.514	-0.536^{*}	-0.888^{**}
EDTA-Cd			1	0.698^{**}	0.492	− 0.526	-0.874^{**}
Fi				1	− 0.067	-0.883^{**}	-0.762^{**}
Fii					1	0.300	-0.592^{*}
Fiii						1	0.074
Fiv							1

Fi, acid-soluble; *Fii*, reducible; *Fiii*, oxidizable; *Fiv*, residual Cd. $^*p < 0.05$, $^{**}p < 0.01$

phosphates, and metal hydroxides, reducing phytoavailability of Cd in soils (Ashrafi et al. 2015; Brown et al. 2005; Gu et al. 2011; Huang et al. 2020; Liang et al. 2014). The BCR analyses indicated that SCKM amendment increased the Cd concentration of residual forms, which indirectly indicated the formation of Cd precipitate in soils. Many previous studies clearly verified the association between elevated soil pH and reduced Cd concentration in soil solution (Bolan et al. 2003; Huang et al. 2020; Ning et al. 2016; Walker et al. 2003). Many previous studies also demonstrated that soil pH was the most important soil property that determines Cd phytoavailability to plants (Adriano 2001; Tang et al. 2006; Toshimitsu et al. 2016; Römkens et al. 2009; Zhu et al. 2016). Therefore, the decrease in concentration of phytoavailable Cd was mainly attributed to the increase of soil pH due to the addition of SCKM amendment (Fig. 5). These results implied that soil pH increase was an effective process that inhibit the Cd uptake by rice plant.

Secondly, the transfer of Cd from the root to the aboveground parts of rice plays an important role in Cd accumulation in rice grain. The SCKM amendment decreased Cd transfer from root to the aboveground parts of rice, which could be another important mechanism in reducing the accumulation of Cd in rice grain. In this pot experiment, $TF_{straw\text{-}grain}$ values were much lower than the $TF_{root\text{-}straw}$ values, indicating that the Cd accumulation in rice grain was largely limited by the lower transfer capacity of Cd from the stem and leave to grain of rice. Correlation analyses indicated that the TF value of Cd from straw to rice grain related significantly ($p < 0.05$) with EDTA-extractable Cd and acid-soluble Cd in soils ($r = 0.583$ and 0.652, respectively). Therefore, the reduced EDTA-extractable and acid-soluble Cd concentration should decease the Cd transfer from root and stem to grain in rice, which could also be an important mechanism in reducing Cd translocation from rice root and stem to grain in rice with respect to SCKM application. The reduction in Cd accumulation within rice grain with respect to SCKM amendment application could be attributed to the inhibition of Cd transfer from root to aboveground parts of rice by retaining the Cd in root tissues of rice.

Thirdly, SCKM amendment application increased the concentrations of exchangeable cations in soils (Table 3). These cations in soils could compete with Cd uptake by rice root. The competition of these cations with Cd reduced the uptake of Cd by rice. Previous studies found that Cd, as a nonessential cation, has not a specific uptake channel in plant. Therefore, the Cd might enter rice cells through uptake system of rice for essential cations (Rizwan et al. 2012; Shi et al. 2010; Zhang et al. 2008). Thus, increased concentrations of essential cations by SCKM amendment application brought about an antagonistic effect on Cd uptake of rice. In addition, the SCKM amendment with high SiO_2 content (about 25%) would certainly cause higher available Si content in soils. Higher Si concentration in soils could decrease Cd uptake and transportation into the shoot and grain of rice. Shi et al. (2010) reported that application of Si fertilizer restricted the transport of Cd from root to shoot of rice. On the other hand, the use of exogenous Si fertilizer could alleviate heavy metal toxicity in plants by co-deposition of metals with silicates in the root cell wall (Rizwan et al. 2012; Zhang et al. 2008). Therefore, the addition of Si in SCKM amendment could decrease the Cd accumulation in rice grain.

Finally, the application of SCKM amendment supplied essential mineral nutrient (Ca, K, and Mg) for rice growth, and reduced aluminum toxicity in acidic soils, which largely improve soil fertility. In this experiment, the use of SCKM amendment significantly increased the biomass and yield of rice grain (Fig. 1), indicating the role of amendment in promoting the rice growth. An ideal soil amendment for practical application should be able to reduce the toxicity of heavy metals and simultaneously offer mineral nutrients for crop growth. Here, on the one hand, SCKM amendment could decrease the phytoavailability of Cd, and the other hand, it eliminates Al toxicity and mineral nutrient deficiencies in acidic soils. The combined effects of SCKM amendments decreased the Cd contamination risk of rice as well as increased the yield of rice grain. Our pot experimental results demonstrated that the SCKM amendment was effective in reducing Cd phytoavailability and accumulation in rice and remedying soil fertility of acidic soils.

In practice, a promising soil amendment to remediate Cd-contaminated soils should be inexpensive and easily applicable. The nature of amendment itself greatly influences the selection and applicability of soil amendment, including cost, rate, acceptance, long-term effectiveness, possibility of secondary pollution, and physicochemical properties of amendment. Among the soil amendments that are used widely in acidic soil, alkaline amendments show high efficiency to immobilize Cd in soils (Bian et al. 2016; Huang et al. 2020; Meng et al. 2019; Ning et al. 2016). However, these amendments should apply at high rate of application and had no significant increasing effect on rice yield. The application of SCKM amendment to Cd contaminated paddy soil can reduce Cd in rice grains and supply Ca, Mg, and Si nutrients, which were most deficient elements in acidic soils. The application of SCKM can also provide a promising remediation technique for potential soil acidification. Therefore, the SCKM was more efficient and more environmentally friendly soil amendments compared with as conventional amendment.

Conclusions

Our pot experiment indicated that SCKM amendment significantly reduced the EDTA-extractable Cd concentration and changed the distribution of chemical forms of Cd in two acidic soils. The SCKM amendment also significantly reduced the translocation of Cd from rice root to above-ground parts of rice. Application of SCKM amendment significantly increased the soil pH value, reduced the Al toxicity, and supplied essential mineral nutrients for rice growth. The SCKM amendment could transform Cd species from the acid-soluble to residual forms, reducing phytoavailabile Cd concentration in soils. The increased soil pH promoted the formation of less phytoavailable phases of Cd, which reduced Cd phytoavailability in soils. The addition of Si and cations brought about by amendment caused an antagonistic effect on Cd uptake of rice. The combined effects of SCKM amendment not only decreased the Cd contamination risk of rice, but also increased the rice yield. Therefore, the application of SCKM amendment could be an effective approach for reducing Cd contamination risk in rice and remedying soil acidity and Al toxicity. Our results recommended that the SCKM amendment was efficient and environmentally friendly soil amendment for safe rice production in Cd-contaminated acidic soils.

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References

Adriano DC (2001) Trace element in terrestrial environments: biogeochemistry, phytoavailability, and risks of metals. Springer, New York

Ahnstrom ZS, Parker DR (1999) Development and assessment of a sequential extraction procedure for the fractionation of soil cadmium. Soil Sci Soc Am J 63:1650–1658

Ashrafi M, Mohamad S, Yusoff I, Hamid FS (2015) Immobilization of Pb, Cd, and Zn in a contaminated soil using eggshell and banana stem amendments: metal leachability and a sequential extraction study. Environ Sci Pollut Res 22:223–230

Bao SD (2008) Soil and agrochemical analyses (in Chinese). China Agriculture Press, Beijing

Bian R, Joseph S, Cui L, Pan G, Li L, Liu X, Zhang A, Rutlidge H, Wong S, Chia C, Marjo C, Gong B, Munroe P, Donne S (2014) A three-year experiment confirms continuous immobilization of cadmium and lead in contaminated paddy field with biochar amendment. J Hazard Mater 272:121–128

Bian R, Li L, Bao D (2016) Cd immobilization in a contaminated rice paddy by inorganic stabilizers of calcium hydroxide and silicon slag and by organic stabilizer of biochar. Environ Sci Pollut Res 23:10028–10036

Bolan NS, Adriano DC, Curtin D (2003) Soil acidification and liming interactions with nutrient and heavy metal transformation and phytoavailability. Adv Agron 78:215–272

Brown S, Christensen B, Lombi E (2005) An inter-laboratory study to test the ability of amendments to reduce the availability of Cd, Pb, and Zn in situ. Environ Pollut 138:34–45

Gu HH, Qiu H, Tian T, Zhan SS, Deng THB, Chaney RL, Wang SZ, Tang YZ, Morel JL, Qiu RL (2011) Mitigation effects of silicon rich amendments on heavy metal accumulation in rice (Oryza sativa L.) planted on multi-metal contaminated acidic soil. Chemosphere 83:1234–1240

Guo JH, Liu XJ, Zhang Y, Shen JL, Han WX, Zhang WF, Christie P, Goulding KWT, Vitousek PM, Zhang FS (2010) Significant acidification in major Chinese croplands. Science 327:1008–1010

Hamid Y, Tang L, Yaseen M (2019) Comparative efficacy of organic and inorganic amendments for cadmium and lead immobilization in contaminated soil under rice-wheat cropping system. Chemosphere 214:259–268

Huang Y, Sheng H, Zhou P, Zhang YZ (2020) Remediation of Cd-contaminated acidic paddy fields with four-year consecutive liming. Ecotoxicol Environ Saf 188:109903. https://doi.org/10.1016/j.ecoenv.2019.109903

Inkham R, Kijjanapanich V, Huttagosol P, Kijjanapanich P (2019) Low-cost alkaline substances for the chemical stabilization of cadmium-contaminated soils. J Environ Manag 250:UNSP 109395. https://doi.org/10.1016/j.jenvman.2019.109395

Juang KW, Ho PC, Yu CH (2012) Short-term effects of compost amendment on the fractionation of cadmium in soil and cadmium accumulation in rice plants. Environ Sci Pollut Res 19:1696–1708

Li JR, Xu YM (2015) Immobilization of Cd in a paddy soil using moisture management and amendment. Chemosphere 122:131–136

Liang X, Han J, Xu Y, Sun Y, Wang L, Tan X (2014) In situ field-scale remediation of Cd polluted paddy soil using sepiolite and palygorskite. Geoderma 235–236:9–18

Liu J, Qian M, Cai G, Yang J, Zhu Q (2007) Uptake and translocation of Cd in different rice cultivars and the relation with Cd accumulation in rice grain. J Hazard Mater 143:443–447

Meng J, Li Z, Wang L, Liu X, Tang C, Chen H, Xu J (2018) Contrasting effects of alkaline amendments on the phytoavailability and uptake of Cd in rice plants in a Cd-contaminated acid paddy soil. Environ Sci Pollut Res 25:8827–8835

Meng L, Huang TH, Shi JC, Chen J, Zhong FL, Wu LS, Xu JM (2019) Decreasing cadmium uptake of rice (Oryza sativa L.) in the cadmium-contaminated paddy field through different cultivars coupling with appropriate soil amendments. J Soils Sediments 19:1788–1798

Ministry of Ecology and Environment of the People's Republic of China (2018) Soil environmental quality, risk control standard for soil contamination of agricultural land. Nation Standard of PRC (GB15618-2018)

Ministry of Environmental Protection of PRC, Ministry of Land and Resources of PRC (2014) The nationwide survey communique of soil pollution. Beijing: Ministry of Environmental Protection of PRC, Ministry of Land and Resources of PRC, 2014-04-17

Nie XX, Duan XL, Zhang MM, Zhang ZY, Liu DB, Zhang FL, Wu MQ, Fan XP, Yang L, Xia XG (2019) Cadmium accumulation, availability, and rice uptake in soils receiving long-term applications of chemical fertilizers and crop straw return. Environ Sci Pollut Res 26:31243–31253

Ning D, Liang Y, Song A, Duan A, Liu Z (2016) In situ stabilization of heavy metals in multiple-metal contaminated paddy soil using different steel slag-based silicon fertilizer. Environ Sci Pollut Res 23:23638–23647

Quevauviller P, Rauret G, Griepink B (1993) Single and sequential extraction in sediments and soils. Int J Environ Anal Chem 51:231–235

Rizwan M, Meunier JD, Keller C (2012) Frontiers | Effect of silicon on reducing cadmium toxicity in durum wheat (Triticum turgidum L. cv. Claudio W.) grown in a soil with aged contamination. J Hazard Mater 209–210:326–334

Rodrigues SM, Cruz N, Coelho C, Henriques B, Carvalho L, Duarte AC, Pereira E, Romkens P (2013) Risk assessment for Cd, Cu, Pb and Zn

in urban soils: chemical availability as the central concept. Environ Pollut 183:234–242
Römkens PFAM, Guo HY, Chu CL, Liu TS, Chiang CF, Koopmans GF (2009) Prediction of cadmium uptake by brown rice and derivation of soil-plant transfer models to improve soil protection guidelines. Environ Pollut 157:2435–2444
Shi G, Cai Q, Liu C, Wu L (2010) Silicon alleviates cadmium toxicity in peanut plants in relation to cadmium distribution and stimulation of antioxidative enzymes. Plant Growth Regul 61:45–52
Tang XY, Zhu YG, Cui YS, Duan J, Tang L (2006) The effect of aging on the bioaccessibility and fractionation of cadmium in some typical soils of China. Environ Int 32:682–689
Toshimitsu H, Hirotomo O, Ayako KK, Tomoyuki M, Ken N, Hidetaka K (2016) Optimal soil Eh, pH, and water management for simultaneously minimizing arsenic and cadmium concentrations in rice grains. Environ Sci Technol 50:4178–4185
Walker DJ, Clemente R, Roig A, Bernal MP (2003) The effects of soil amendments on heavy metal phytoavailability in two contaminated Mediterranean soils. Environ Pollut 122:303–312
Wang M, Chen W, Peng C (2016) Risk assessment of Cd polluted paddy soils in the industrial and township areas in Hunan, Southern China. Chemosphere 144:303–312
Zhang C, Wang L, Nie Q, Zhang W, Zhang F (2008) Long-term effects of exogenous silicon on cadmium translocation and toxicity in rice (Oryza sativa L.). Environ Exp Bot 62:300–307
Zhou H, Zhou X, Zeng M, Liao BH, Liu L, Yang WT, Wu YM, Qiu QY, Wang YJ (2014) Effects of combined amendments on heavy metal accumulation in rice (Oryza sativa L.) planted on contaminated paddy soil. Ecotoxicol Environ Saf 101:226–232
Zhu HH, Chen C, Xu C, Zhu Q, Huang D (2016) Effects of soil acidification and liming on the phytoavailability of cadmium in paddy soils of central subtropical China. Environ Pollut 219:99–106