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RESEARCH PAPER

Evaluation of Calcium Oxide of Quicklime and Si–Ca–Mg Fertilizer for Remediation of Cd Uptake in Rice Plants and Cd Mobilization in Two Typical Cd-Polluted Paddy Soils

Xin-Yang Li[1,2] · Jian Long[1,2] · Pei-Qin Peng[1,2] · Qi Chen[1,2] · Xia Dong[1,2] · Kai Jiang[1,2] · Hong-Bo Hou[1,2] · Bo-Han Liao[1,2]

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Abstract

Lime and Si fertilizer are effective amendments for alleviating Cd accumulation in crops. In this study, two Cd-polluted typical soils from different regions in China were sampled to conduct a pot experiment. The effects of two soil amendments [calcium oxide of quicklime (SH) and Si–Ca–Mg fertilizer (GF)] on the distribution of Cd fractions in soil with and without rice-planting treatment and on Cd uptake and accumulation in rice were investigated. The results showed that SH and GF application significantly reduced Cd accumulation in rice in YSS and GSS, and that the maximum Cd reduction in GSS reached 319 μg pot^{-1} with SH treatment. SH and GF significantly decreased and increased, respectively, the proportions of Acid-Cd and Res-Cd in the soil. Rice-planting treatment activated Res-Cd compared with no rice-planting treatment, and SH and GF restrained the remobilization process. Significant positive correlations were found between Res-Cd remobilization rates in soil and Cd content in brown rice. Multiple regression revealed that applying GF at dosages of 1.296 g kg^{-1} and 1.246 g kg^{-1} in YCS and GSS, respectively, was an ideal method to control soil acidity. This study highlighted the view that Res-Cd remobilization provoked by rice plays a considerable role in influencing Cd bioavailability in the soil, that soil type should be considered as a factor when applying soil amendments to contaminated soils, and that soil amendment dosages should vary according to soil type.

Keywords Calcium oxide of quicklime · Si–Ca–Mg fertilizer · Bioavailability · Soil types · Cd · Remobilization

Introduction

Heavy-metal contamination of soils has been a severe environmental problem around the world in the past few decades due to anthropogenic activities such as overuse of pesticides and chemical fertilizers in agriculture and improper smelting in the industry (Zhao et al. 2015). Cadmium (Cd) has been a serious concern because of its high toxicity, which threatens arable land and poses a high health risk through soil–food chain transfer (Meharg et al. 2013). Rice (*Oryza sativa* L.) is the staple food of more than half of the world's population and has been a major food for people in southern China for a long time (Rizwan et al. 2016). Cd can be readily taken up by rice and translocated in rice tissues. Many studies have shown that the Cd concentration in rice depends highly on the presence of certain forms or binding states of Cd in soil rather than on the total Cd concentration, which refers to the level of soil contamination (El-Naggar et al. 2018; Yu et al. 2016; Zhou et al. 2014).

It has been widely reported that soil acidification has accelerated in recent decades (Guo et al. 2010). Soil acidification, which is generally indicated by soil pH decline, has dramatically increased Cd bioavailability and mobility in soil and Cd uptake and accumulation in rice (Wang et al. 2015; Zeng et al. 2011). Furthermore, rhizospheric soil pH has directly influenced Cd behavior in the rhizosphere (Li et al. 2009). Cieśliński et al. (1998) showed that plant roots secreted a large amount of macromolecular organic acid into the soil rhizosphere, which greatly increased the mobilization of insoluble Cd in the root soil by rice and had a significant positive correlation with Cd content in plants.

✉ Pei-Qin Peng
pqpeng123@126.com

[1] College of Environment Science and Engineering, Central South University of Forestry and Technology, Changsha 410004, China

[2] Hunan Engineering Laboratory for Control of Rice Quality and Safety, Central South University of Forestry and Technology, Changsha 410004, China

Kidd et al. (2009) showed that plant-induced remobilization and bioavailability of insoluble Cd is sharply influenced by soil pH. Soil amendments such as lime and Si fertilizer are popular materials to mitigate soil acidification. Lime can increase soil pH and thus restrict Cd mobility by promoting the concentration of adsorptive Cd, which could reduce Cd accumulation in rice plants. For instance, Cd content in rice tissues could be reduced by 20–37.5% and forms of Cd that are carbonated or bound to Fe/Mn could be significantly increased by applying lime at 150 g m^{-2} (Zhu et al. 2010). Bian et al. (2016) found that applying calcium hydroxide decreased the concentration of $CaCl_2$-extractable Cd in soil by 67–76% through increasing soil pH. Huang et al. (2018) found that liming enhanced soil pH and decreased Cd concentration in rice grains by 45.8%. Wei et al. (2017) found that Si fertilizer decreased total Cd content in rice leaves and grains by 11.4–51.9%. In general, two major mechanisms by which Si fertilizer reduces Cd transformation in soil–rice systems have been accepted. The first is that Si fertilizer increases soil pH and reduces Cd mobility in soil (Babu and Nagabovanalli 2017). The second is a Si-induced restriction of root–shoot transport of Cd through Si–Cd precipitation in the cytoderm, thus reducing Cd accumulation in rice grains (Liu et al. 2013).

However, a series of studies have demonstrated that soil type is an important factor affecting the effectiveness of Cd immobilization (Bolan et al. 2014). Moreover, different treatments have different abilities to amend the Cd-contaminated soil, and the use of amendments should also consider the risk of soil alkalinity (Roig et al. 2012). According to Tsadilas et al. (2005), lime applied at 3000 kg $Ca(OH)_2$ ha^{-1} in typical haploxeralf soil may increase soil pH by 0.8 units and decrease available Cd by 40%. In some cases, liming may actually increase Cd accumulation in rice in a typical Thai soil. Therefore, the effect of soil type must be considered when applying soil amendments to the Cd-contaminated soil.

In this study, a rice cultivation pot experiment was carried out in two typical paddy soils (yellow clayey soil and granitic sandy soil). The objectives of the present study were (1) to investigate Cd uptake, accumulation in rice, and the distribution of Cd fractions in different parent material-derived soils influenced by soil amendments (SH and GF), (2) to assess the effect of SH and GF on remobilization of insoluble Cd in soils by rice, and (3) to optimize amending measures in different parent material-derived soils by evaluating the differences between liming and applying Si–Ca–Mg fertilizer on different parent material-derived soils and exploring the probable mechanisms of any differences.

Materials and Methods

Test Materials

Granitic sandy soil (GSS) from a paddy field located in Lukou Town in Changsha City, China (28°26′46″N, 113°19′13″E) and yellow clayey soil (YCS) from a paddy field located in Tuojia Village, Jinjing Town in Changsha City, China (28°33′31″N, 113°20′5″E) were chosen for this study. The test soils were collected from the plowed layer (0–20 cm) of paddy fields, air-dried, crushed, passed through a 2-mm sieve, and mixed thoroughly before use. Table 1 gives the characteristics of the paddy soils. The pot experiments were carried out in the experimental facilities of the Life Science Building of the Central South University of Forestry and Technology. The mean annual temperature was between 16.8 and 17.2 °C, the mean annual precipitation was between 1200 and 1700 mm, and the frost-free period was ~ 295 days, with broad visibility and ample sunlight.

Prepared dry soil (4.0 kg) was placed in each cylindrical plastic pot (200 mm in diameter and 200 mm deep) with five replications. As N fertilizer, urea as a base fertilizer was applied at 0.15 g kg^{-1} into the soil in each pot 1 week before transplanting, and urea was also applied as topdressing. Urea was applied at 0.1 g kg^{-1}, and K_2CO_3 was used at 0.15 g kg^{-1} after 15-day anthropogenic mellowing. Then, the Xiang Zaoxian45 (ZX45) rice cultivar was transplanted into the pots, with two seedlings per pot, and identical pots with no rice planted were prepared. During the whole rice-growing season, the soil was continuously submerged under 2 cm of water. Two soil amendments [Si–Ca–Mg fertilizer (GF), which was provided by the Shandong Laifeng Agricultural Science and Technology Corporation, and calcium oxide of quicklime (SH), which was applied as CaO powder] were separately applied to the soil in all six pots 10 days after rice planting. The basic characteristics of the two amendments were as follows: pH was 12.2; total contents of CaO, K_2O, MgO, and SiO_2 were 30%, 8%, 9%, and 20%, respectively; Cd concentration was 0.08 mg kg^{-1} (Si–Ca–Mg fertilizer),

Table 1 Basic physical and chemical properties of soil

Soil types	Parent material	Cd (mg kg^{-1})	pH values	CEC (Cmol kg^{-1})	OM (g kg^{-1})	Particle (%)		
						Clay	Silt	Sand
YCS	Plate shale	1.09	6.23	9.07	14.24	25.37	35.86	38.77
GSS	Granitic	1.05	5.45	7.88	20.88	14.28	29.45	56.27

CEC cation exchange capacity, *OM* organic matter, *YCS* yellow-clayed soil, *GSS* granitic sandy soil and the pH of calcium oxide of quicklime (CaO powder) was 12.8. Five SH and GF treatments were designated as: Control (only soil), GF1 (1 g/kg GF), GF1.5 (1.5 g/kg GF), SH1 (1 g/kg SH), and SH1.5 (1.5 g/kg SH).

Sampling and Analysis

Sampling

Soil and plant samples were collected from each pot after 90 days of rice growth on October 9 during the maturity period. The soil samples were sealed in plastic bags and transported to the laboratory, where plant detritus and other fragments were removed. After air-drying and crushing, the soil samples were ground and passed through a 10-mesh sieve for analysis of pH, CEC, and clay content. A portion of the soil in each sample was further ground to pass a 100-mesh sieve for the analysis of extractable metal concentration. The rice plants were washed with both tap and deionized water to remove soil and then placed in a 105 °C drying oven for 30 min, followed by a 70 °C drying oven until the weight of the sample remained constant. Five tissue types (root, shoot, leaf, husk, and brown rice) of the rice plant were separated, and the dry weights of different tissues were measured. The plant samples were ground, sieved through a 100-mesh sieve, and then kept in clean polyethylene containers for further analysis.

Analysis

Analysis of soil properties was conducted following procedures described elsewhere (Liu et al. 2015). Soil pH was measured using a pH meter (PHS-3C, REX, Shanghai, China) with a water–soil ratio of 2.5:1 (*v*:*m*). The soil samples were acid-digested with aqua regia and perchloric acid to obtain the total Cd concentration. The fractions of soil Cd were obtained according to the modified BCR sequential extraction scheme as described in Li et al. (2016). Cd concentrations in all extracts were analyzed with flame atomic absorption spectroscopy (AAS: ICE-3500, Thermos, Waltham, USA). The detection limit was ~ 0.001 mg/L. Samples below this limit were measured by graphite furnace AAS (Thermos). Analysis of various rice-plant tissues was conducted using the dry ashing method (Wang et al. 2014), and the Cd concentrations in different tissues were analyzed with graphite furnace AAS.

Statistical Analysis

All data were analyzed using the LSD test at a significance level of p (Pearson's correlation coefficient) < 0.05 (using SPSS version 22.0) to examine the differences between the two soil parent materials and the two amendments. All figures were produced using Origin version 9.0.

Results

Effects of Soil Amendments on Rice Biomass

Figure 1 shows the biomass of rice cultivar ZX45 planted in the two typical Cd-contaminated soils (GSS and YCS). Rice in both soils was capable of growing and gradually fruiting under all the five treatments. The biomass of rice (roots, stems, leaves, husks, and brown rice) on GSS was significantly higher than on YCS under the Control treatment, whereas the biomass of rice on GSS was significantly lower than on YCS under the SH and GF treatments.

The variation in biomass under different treatments showed obvious differences between YCS and GSS. The biomass was significantly elevated under the GF and SH treatments compared with the Control treatment and reached a maximum under the GF1.5 treatment of 588.79 g pot^{-1} on YCS. For GSS, however, GF and SH reduced the biomass, which reached a minimum under the SH1.5 treatment of 301.17 g pot^{-1}. Moreover, the biomass of stems was enormously influenced by the addition of SH and GF both on YCS and GSS, although variation in the biomass of roots, leaves, and husks in both YCS and GSS was minimal. The biomass of brown rice on GSS soil was decreased from 94.11 to 70.88 g pot^{-1}, but there was scarcely any variation in brown rice biomass on YCS.

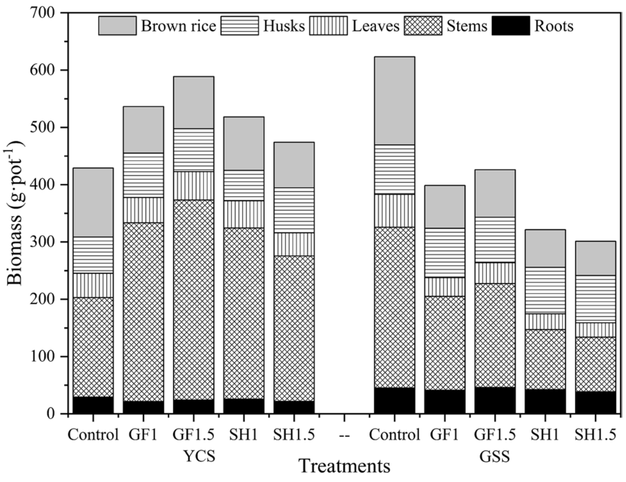

Fig. 1 Biomass of rice cultivar ZX45 in YCS and GSS under GF and SH treatments

Effects of Soil Amendments on Cd Accumulation in Rice Tissues

Figure 2 shows the Cd concentrations obtained in rice tissues (roots, stems, leaves, husks, and brown rice). For the Control treatment, Cd concentrations in tissues followed the order: roots > stems > leaves > husks > brown rice on YCS, whereas Cd concentrations in husks were higher than in leaves on GSS. SH treatments, to some extent, enhanced Cd concentrations in roots. At the other extreme, were the GF treatments, which actually inhibited Cd accumulation in roots. Cd concentrations in roots increased and decreased by 9.6–54.5% and 29.3–42.5% with SH and GF treatments, respectively, on YCS, and by 2.1–8.7% and 39.3–51.5% for the same treatments on GSS, respectively. SH and GF treatments significantly reduced Cd concentrations in stems, leaves, husks, and brown rice on both YCS and GSS.

To assess the ability of SH and GF to inhibit Cd accumulation in rice on these two typical soils, Cd amounts accumulating in rice tissues (roots, stems, leaves, husks, and brown rice) were calculated from Cd concentrations multiplied by the corresponding rice tissue biomasses (Fig. 3). The amounts of accumulated Cd in rice plants under GF and SH treatments were significantly lower than under the Control treatment on GSS, although no significant influence of the GF and SH treatments was found compared with Control. The maximum Cd reduction on GSS reached 319 μg pot^{-1} with SH1.5 treatment. For YCS, the SH and GF treatments on average increased the amounts of Cd in stems by 16.5% and 41.3%, respectively. For GSS, the SH and GF treatments on average decreased the amounts of Cd in stems by 85.2% and 65.1%, respectively. Compared with Control, SH and GF reduced the amounts of Cd in roots, leaves, husks, and brown rice. The amounts of Cd in brown rice decreased on average by 55.8% and 64.5% with the SH and GF treatments on YCS and by 7.57% and 73.4% on GSS, respectively.

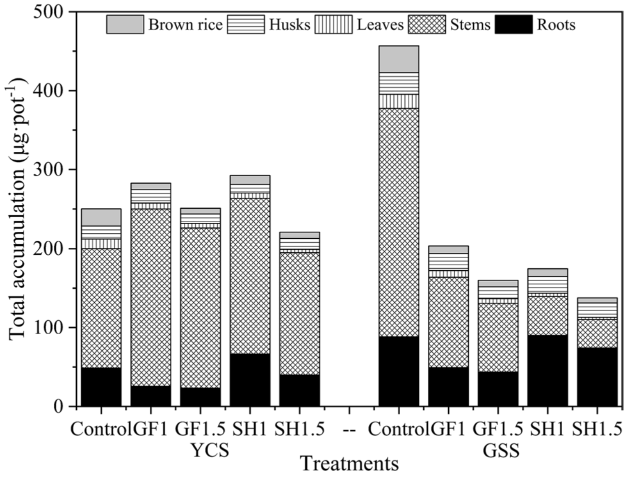

Fig. 3 Amounts of accumulated Cd in rice tissues in YCS and GSS under GF and SH treatments

Effects of Soil Amendments on the Distribution of Cd Fractions in Soils

Figure 4 shows the distributions of Cd fractions on YCS and GSS under GF and SH applied with and without rice-planting treatment. Compared with Control, SH and GF significantly enhanced and decreased the proportion of Res-Cd and Acid-Cd of YCS and GSS both with and without rice-planting treatment. With no rice-planting treatment, SH and GF on average decreased the percentages of Acid-Cd by

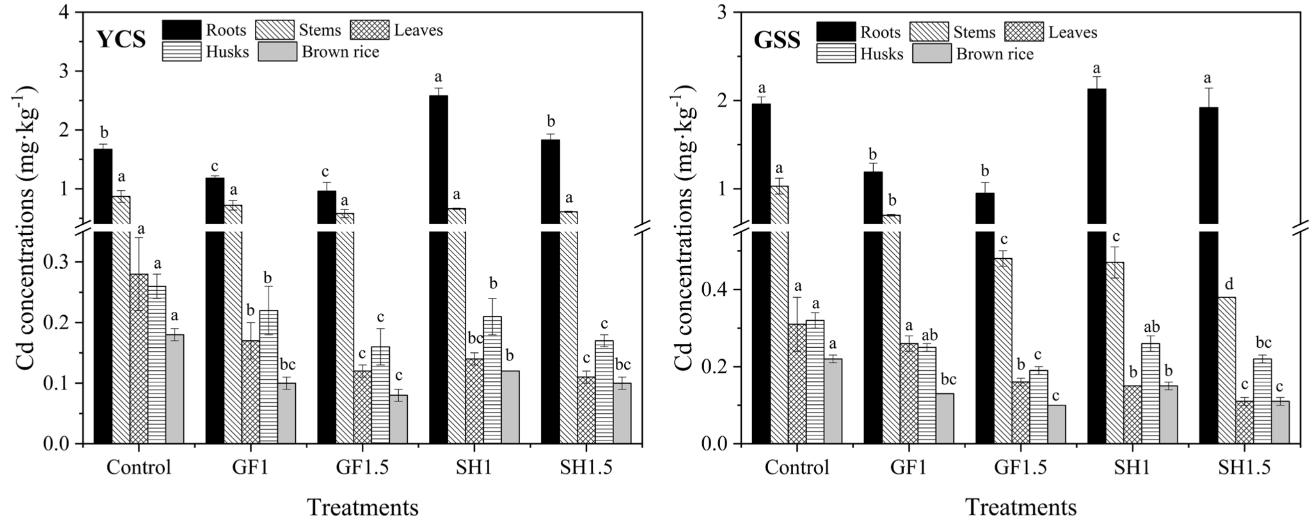

Fig. 2 Cd concentrations in rice tissues in YCS and GSS under GF and SH treatments. Values followed by different lowercase letters in the same rice tissues under different amendment treatments are significantly different at $p < 0.05$. Error bars are standard deviations

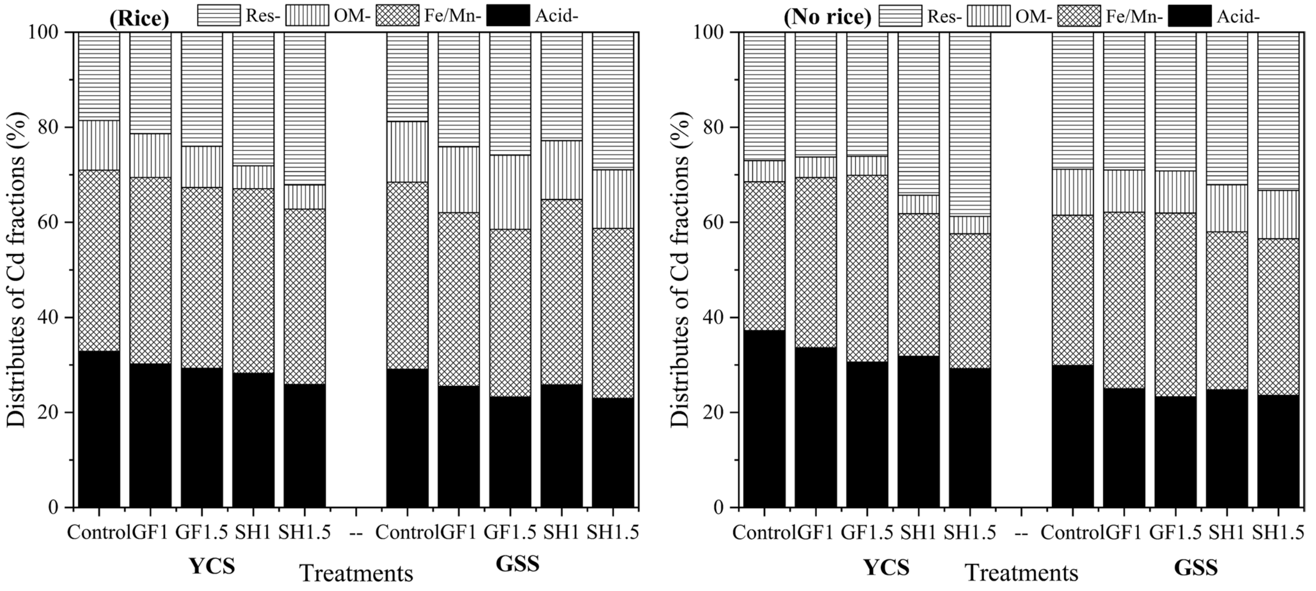

Fig. 4 Distributions of Cd fractions in YCS and GSS under GF and SH applied with and without rice-planting treatment

18.0% and 13.8% on YCS, respectively, and by 19.1% and 19.2% on GSS, respectively. SH increased the percentages of Res-Cd by 35.2% and 13.3% on YCS and GSS, respectively. The effects of SH and GF on the percentages of Fe/Mn–Cd and OM-Cd on YCS and GSS were imperceptible. With rice-planting treatment, compared with Control, SH and GF on average decreased the proportion of Acid-Cd by 17.6% and 9.4% on YCS and by 16.2% and 16.3% on GSS, respectively. SH and GF on average increased the proportion of Res-Cd by 62.3% and 22.0% on YCS and by 37.8% and 33.0% on GSS, respectively. Furthermore, the percentages of OM-Cd were reduced by 52.7% on average with SH treatments on YCS, but variation in the proportion of Fe/Mn–Cd was imperceptible on both YCS and GSS.

Remobilization of Cd in the Soil–Rice System

Figure 5 shows the remobilization rates of Res-Cd from rice-planting treatments on YCS and GSS. Compared with the absence of rice-planting treatment, the amounts of Res-Cd significantly increased after rice were planted. This might indicate an accelerating effect of rice on the mobilization of insoluble Cd in soils. The increment of Res-Cd reached almost 50% on both YCS and GSS. The remobilization rates were significantly influenced by SH and GF addition in these two soils. However, a remarkable decline was found with SH and GF treatments on GSS. SH and GF resulted in approximately 36.6% and 49.9% lower remobilization of Res-Cd than Control on GSS. For YCS, SH and GF resulted in approximately 31.7% and 39.3% lower remobilization of Res-Cd than Control. Therefore, the conclusions could be drawn that rice played an important role in mobilizing insoluble Cd in soils and that soil amendments (SH and GF) restricted the remobilization process.

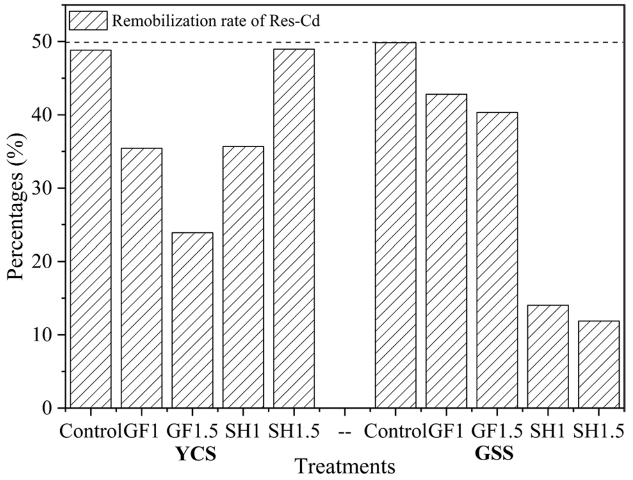

Fig. 5 Res-Cd remobilization rates from rice-planting treatments in YCS and GSS. Remobilized rates of Control, SH, and GF treatments were calculated using the formula $(A_{nri}-A_{ri})/A_{nri} \times 100\%$, where A_r and A_{nr} were the amounts of Res-Cd with and without rice-planting treatment and the subscript *i* refers to one of the five treatments

Effects of Soil Amendments on Soil Physiochemical Properties

Soil physiochemical characteristics changed under different treatments (Table 2). Soil pH and CEC gradually increased with the addition of SH and GF. Compared with Control, SH1 on average increased the pH of YCS and GSS by 1.03 and 1.30 units, respectively, and the CEC by 3.27 and 2.90

Cmol kg^{-1}, respectively. SH1.5 increased the soil pH of YCS and GSS by 1.06 and 1.35 units, respectively, and the CEC by 3.32 and 3.22 Cmol kg^{-1}, respectively. The pH of YCS and GSS under the GF1 treatment was increased by 1.82 and 1.89 units, respectively, and the CEC by 1.82 and 2.62 Cmol kg^{-1}, respectively. The pH of YCS and GSS under the GF1.5 treatment was increased by 1.84 and 1.93 units, respectively, and the CEC by 1.97 and 2.74 Cmol kg^{-1}, respectively. Furthermore, higher additions of GF and SH resulted in higher pH and CEC, and the SH treatments had more influence than the GF treatments on pH values and CEC in the two types of soil.

Influence of Remobilized Cd on the Accumulation of Cd in Brown Rice

Under the SH and GF treatments, the Pearson's correlation coefficients between pH, CEC, and Cd in brown rice and the Res-Cd remobilization rates in the two soils were determined to assess the relationship between Cd accumulation in brown rice and Cd remobilization in soils; these relationships are summarized in Table 3. The results showed that strongly positive and significant correlations were found between Res-Cd remobilization rates and Cd contents in brown rice (YCS: $r = 0.960$, $p < 0.01$; GSS: $r = 0.976$, $p < 0.01$). Significant negative correlations were also found between pH and Cd in brown rice (YCS: $r = -0.920$, $p < 0.05$; GSS: $r = -0.903$, $p < 0.05$). Furthermore, a significant negative correlation was found between CEC in GSS and Cd contents in brown rice ($r = -0.910$, $p < 0.05$). Therefore, Res-Cd remobilization had an extremely significant effect on Cd accumulation in brown rice, an observation that should be strongly emphasized.

Determining the Application Dosages of SH and GF

The preceding discussion summarized the positive correlation between soil pH and Res-Cd remobilization rate. The practical application presented for applying soil amendments (SH and GF) was to control soil acidity. However, there were restrictions on applying the same doses of soil amendment on different types of soil or applying different soil amendments on the same type of soil. Table 4 shows the results of multiple regression analyses based on the correlation

Table 2 pH and CEC values in soils amended with SH and GF treatments (mean value ± standard deviation)

Treatments	pH		CEC (Cmol kg^{-1})	
	YCS	GSS	YCS	GSS
Control	4.87 ± 0.08e*	4.87 ± 0.04d	9.11 ± 0.03d	8.90 ± 0.34e
GF1	6.70 ± 0.02b	6.76 ± 0.05a	10.93 ± 0.05bc	11.28 ± 0.12cd
GF1.5	6.78 ± 0.02a	6.80 ± 0.07a	11.08 ± 0.09b	11.40 ± 0.08bc
SH1	5.90 ± 0.04cd	6.16 ± 0.02bc	12.37 ± 0.35a	11.56 ± 0.10b
SH1.5	5.93 ± 0.03c	6.21 ± 0.01b	12.43 ± 0.29a	11.88 ± 0.24a

*Values followed by different lowercase letters in the same column are significantly different at $p < 0.05$

Table 3 Correlation analysis between Cd accumulation in brown rice and remobilization of Res-Cd

	YCS		GSS	
	$Cd_{brown\ rice}$	Remobilization rate	$Cd_{brown\ rice}$	Remobilization rate
pH	−0.920*	−0.813	−0.903*	−0.864
CEC	−0.672	−0.645	−0.910*	−0.815
$Cd_{brown\ rice}$	1	0.960**	1	0.976**

*, **Values followed by diferent lowercase letters in the same column are significantly different at $p < 0.05$ and $p < 0.01$, respectively

Table 4 Relationship between soil pH and required dose of soil amendments

Treatments	YCS		GSS	
	Regression equations	Applying dosage (g/kg)	Regression equations	Applying dosage (g/kg)
SH	$Y = 1.398X + 4.838$	1.546	$Y = 1.293X + 1.930$	3.921
GF	$Y = 4.803X + 0.777$	1.296	$Y = 4.919X + 0.870$	1.246

Y means soil pH and *X* means the applying doses of soil acidity amendments between soil pH and the applied dose of soil amendment. It was clear from the regression equations that the required dose of soil amendment to enhance soil pH to 7 differed by soil type. In YCS, the liming dose was 1.296 g kg^{-1}, and the required dose of GF was 1.546 g kg^{-1}. For GSS, the liming dose was 1.246 g kg^{-1}, and the required dose of GF was 3.921 g kg^{-1}.

Discussion

The data obtained have shown that the application of SH and GF reduced rice biomass on GSS, but had no significant impact on YCS. This may reflect the difference between YCS and GSS. Higher application of SH is generally suitable for clay-abundant soils (So and Ringrose-Voase 2000). In the present study, the application dose of 1 g kg^{-1} of SH and GF may have been appropriate for YCS, but excessive for GSS. The proposed application dose of calcium oxide of quicklime on sandy soil, where the pH typically ranges from 5.0 to 6.5, was 75 kg ha^{-1}. An excess of SH and GF applied to soil may suppress P availability and thus reduced rice growth (Ai et al. 2015). Furthermore, 1-year pot experiments should be carried out to confirm the effects of calcium oxide of quicklime and Si–Ca–Mg fertilizer on rice biomass on different soils.

The results obtained herein showed that SH and GF application reduced Cd concentration and total accumulation in rice plants (Fig. 2). In general, soil properties such as pH, CEC, clay content, soil moisture, and temperature affect Cd transformation in the soil–rice system and Cd uptake and accumulation in rice (Husson 2012; Liu et al. 2015). Of these, pH has been considered as a major factor influencing Cd speciation, solubility, and mobility in soil, as well as determining Cd accumulation in rice (Chen et al. 2017; He et al. 2015; Kosolsaksakul et al. 2014; Qi et al. 2018). In the present study, applying soil amendments significantly increased soil pH (Table 2). An increase in soil pH may enhance the concentration of OH^- in the soil solution, which may reduce potential desorption of Cd^{2+} (Du Laing et al. 2009; Li et al. 2016). Significant and negative correlations between pH and Cd mobility in soils have been widely reported (Rafiq et al. 2014). An increase in pH leads to deprotonation of hydroxyl groups on the surface of iron and aluminum oxides, leading to an increase in the negative charge of the soil colloid surface (Huang et al. 2014; Zeng et al. 2011). More strongly negative charges can attract more Cd^{2+} toward the soil surface through electrostatic attraction (Calace et al. 2009). Furthermore, an increase in soil pH promotes the transformation of Cd^{2+} to some complexes with stable forms and manganese oxides, which then enhance sorption on the soil surface (Wang and Chen 2015; Zhao et al. 2014). By these means, Cd mobility and solubility in the soil can be enhanced. SH and GF provide large amounts of Ca, Mg, and Si, which could compete for Cd for uptake by rice. In addition, Si was found to crosslink with cell wall hemicelluloses. It has been postulated that the negative charge of Si complexes in the cell wall may enhance Cd binding and thereby inhibit Cd translocation within the rice plant (Liu et al. 2013; Ma et al. 2015).

It is well known that the bioavailable fraction of Cd can be easily utilized by rice. The present study showed that the proportion of Acid-Cd and Res-Cd decreased and increased in soils with SH and GF applied compared to the Control (Fig. 3). The increased pH under SH and GF treatments produced OH^- ions, which precipitated with Cd, reducing the bioavailable fraction of Cd (Kim et al. 2017). In addition, SH and GF contain large numbers of cations (Ca^{2+}, Mg^{2+}, and Si^{2+}). Application of SH and GF increased ion-exchange capability, surface complexation reactions, sorption by soil colloids, and competition between soil cations and Cd (Yang et al. 2017). The percentages of Res-Cd without rice-planting treatment were significantly higher than with rice-planting treatment, which might be attributed to activation of insoluble Cd in rice. Rice rhizospheric microorganisms play a vital role in transforming Cd, thereby influencing the behavior of insoluble Cd, which is biotransformed by its release from the solid phase into the solution phase (Bolan et al. 2014). This study showed extremely significant positive correlations between Res-Cd remobilization rates and Cd accumulation in brown rice. Rice root exudates, especially organic acids that favor chelation of insoluble Cd in soils, improving their bioavailability and solubility, thus enhance Cd uptake and accumulation in brown rice (Liu et al. 2003). Furthermore, SH and GF effectively restrained Res-Cd remobilization. Siderophores are considered as an important indicator of heavy-metal mobilization in soil–plant systems (Li et al. 2009). Lower activity of the soil microbe community stimulates the formation of siderophores, which enhance Cd mobility (Ashraf et al. 2017). Application of SH and GF elevates soil pH and ameliorates the activity of soil microorganisms, which might have reduced Res-Cd mobilization of in soil.

The foregoing discussion highlights the suppression effect of SH and GF on the proportion of soluble Cd, the remobilization of insoluble Cd in the soil, and the uptake of Cd in rice plants. However, greater effectiveness was observed in GSS than in YCS. The differences in amending effectiveness between soil types may also be attributed to differences between the parent materials of the two types of soil. In this study, SH and GF enhanced the proportion of clay by 41.4% and 49.9% on average in YCS and GSS, respectively (Fig. 6). SH and GF provide Si^{2+} and Ca^{2+}, which bind with organic and inorganic colloids and, thus, contribute to the formation of soil aggregates. This provides an opportunity to increase the clay content in YCS and GSS.

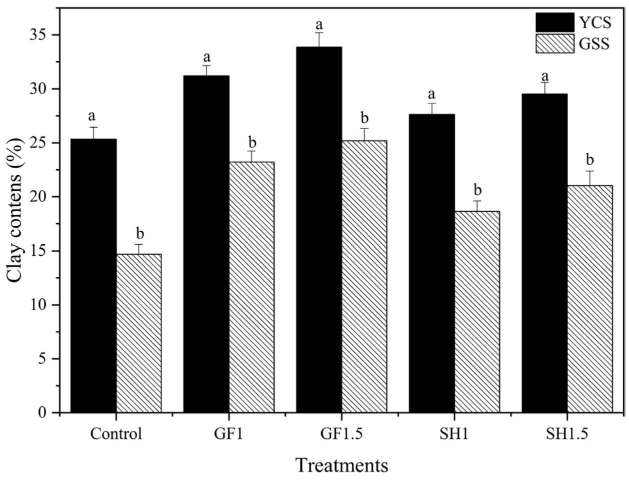

Fig. 6 Clay content in soils amended with SH and GF treatments. Different lowercase letters indicate a significant difference ($p < 0.05$) for the same amendment treatment between YCS and GSS

In general, soil clay content provides a measure of available sorption sites, and therefore, higher clay content could promote Cd sorption (Rafiq et al. 2014). In addition, soil CEC may influence Cd distribution onto the surface of soil solids in solution, which could affect Cd accumulation in rice plants. This study found that applying SH and GF increased ion intensity and elevated CEC content. Simultaneous GF and SH treatments enhanced CEC content more strongly in GSS than in YCS (Table 2).

In summary, SH and GF restrict Cd bioavailability, not only by reducing and enhancing the proportions of soluble and insoluble Cd in the soil, but also by suppressing remobilization of insoluble Cd as affected by rice. The required doses of SH and GF should be considered in light of the differences among soil types. Note that this study was a 1-year pot experiment, which may not reflect the effectiveness of applying SH and GF in fields. Consequently, multiple-site and multiple-year studies should be carried out in coordination with field studies to verify and expand the results. In addition, further studies are also needed on the differences among rice cultivars and their relationship with uptake and transport of specific insoluble Cd compounds.

Conclusions

SH and GF effectively decreased Cd bioavailability in soil. The mechanism of reducing Cd bioavailability in soil by applying SH and GF is that these amendments contribute to lower and higher proportions of soluble and insoluble Cd in soil and a reduction of remobilization of insoluble Cd in the soil, thus decreasing Cd uptake in rice plants. Furthermore, the amending effectiveness in GSS was significantly higher than in YCS. SH and GF application rates of 1.546 and 1.296 g kg^{-1}, respectively, in YCS, and 3.921 and 1.246 g kg^{-1} in GSS, respectively, were optimal for controlling soil pH to a neutral level (7.0). This condition was most favorable to immobilizing soluble Cd and suppressing insoluble Cd remobilization in the soil. Consequently, amendment quantities and soil types should be considered in the remediation of Cd-contaminated rice fields.

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