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Effectiveness of simultaneous applications of lime and zinc/iron foliar sprays to minimize cadmium accumulation in rice

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ABSTRACT

Due to the large area of Cd-contaminated paddy soils worldwide, low-cost measures to reduce the accumulation of Cd in rice plant are necessary. A field experiment was therefore conducted to investigate the reducing effect of lime combined with foliar applications of Zn ($ZnSO_4$) or Fe ($EDTA \cdot Na_2Fe$) on Cd concentrations in brown rice on a Cd-contaminated paddy soil. The results indicated that liming alone or in combination with foliar sprays of Zn or Fe increased the soil pH by 0.27–0.63 units. However, limited effects of lime or lime combined with foliar applications of Zn/Fe on soil DTPA-extractable Cd, rice grain and rice straw biomass were observed. Liming alone significantly reduced the Cd concentration in brown rice and rice straw by 31.8% and 42.3%, respectively. The Cd concentrations in brown rice decreased by 25.5% and 65.4% and in rice straw by 53.0% and 68.1% after liming combined with foliar applications of Fe and Zn, respectively. In contrast, liming combined with foliar spraying of Fe significantly increased the transfer ratio of Cd from the rice straw to the grain. As a low-cost technique, lime application combined with foliar application of $ZnSO_4$ could be recommended for the remediation of Cd-contaminated paddy soils.

1. Introduction

Rice (*Oryza sativa* L.) is a staple food for approximately half of the world's population and is one of the most widely planted cereal corps worldwide, especially in Asia (Li et al., 2017). However, due to human activities such as mining, smelting, and applying sludge and fertilizer, the pollution of cadmium (Cd) in paddy soils is widespread (Wang et al., 2015). For example, according to Chinese soil environmental quality limits (EQL), approximately 7.0% of agricultural soils are contaminated with Cd; these soils are distributed mainly in paddy regions (He et al., 2017). As a result, more than 10% of the brown rice in China was found to be contaminated with Cd (Li and Xu, 2015). Further, this problem is found not only in China and other Asian countries but also in African and Latin American countries, where rice production and consumption have been growing rapidly (Hu et al., 2016).

To remove the excessive Cd in soils, countermeasures against Cd-contaminated soils such as soil removal and replacement (Uraguchi and Fujiwara, 2012), soil turnover and dilution (Hseu et al., 2010), soil dressing (Arao et al., 2010), chemical washing (Chaney et al., 2004), and phytoremediation (Wang et al., 2011) have been proposed. Although soil pollution by Cd is reversible, these measures are costly and time consuming and may impact crop production after remediation (Hu et al., 2016). As such, low-cost but effective approaches such as in situ immobilization and applications of micronutrient elements can reduce the accumulation of Cd in rice grain (Puschenreiter et al., 2005).

Lime is a common amendment that is widely used to reduce the bioavailability of Cd in paddy soils. Our previous studies showed that quicklime applied at a rate of 900–1500 kg hm^{-2} significantly reduced the accumulation of Cd in brown rice (Huang et al., 2000; Zhu et al., 2010, 2016; He et al., 2017). Liming experiments conducted on soils with a total Cd content of 0.12–1.25 mg kg^{-1} at 33 sites indicated that the average Cd concentration in brown rice decreased from 0.34 to 0.22 mg kg^{-1} (Zhu et al., 2016). Although the Cd concentration in brown rice decreased by 35.3%, the mean Cd concentration was still slightly higher than the standard allowable Cd concentration in brown rice implemented by the China government (0.20 mg kg^{-1}). Similarly, application of lime that significantly reduce Cd accumulations in rice grain while not meeting Cd limiting standards have also been reported

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(Bian et al., 2016; L.F. Li et al., 2016, M. Li et al., 2016; Xiao et al., 2017). In these cases, lime could be applied to slightly to moderately contaminated paddy soil to immobilize Cd (Hu et al., 2016).

Zinc (Zn) and iron (Fe) are both reported to reduce the accumulation of Cd in rice plant. Previous studies have indicated that foliar application of Zn can effectively reduce the content of Cd in rice plants. For example, Fahad et al. (2015) conducted a two-year field experiment on an alkalescent Cd-contaminated soil and found that foliar application of $ZnSO_4$ on five different rice cultivars at the panicle initiation stage and milky stage significantly reduced the Cd concentration in brown rice by more than 17%. Similar Cd accumulation reduction effects after foliar application of $ZnSO_4$ on rice growing on slightly acidic Cd-contaminated soil were reported by Hu et al. (2011). However, conflicting effects on Cd accumulation in rice plant after foliar application of Fe were reported by previous researchers. Bashir et al. (2018) found that foliar application of Fe-lysine (1.5–7.5 $mg\,L^{-1}$) significantly reduced the concentration of Cd in rice shoots and roots by 16–53% and 17–34%, respectively. While, Shao et al. (2008) reported that soil application of $EDTA{\cdot}Na_2Fe$ significantly reduced the Cd concentration in brown rice by more than 75%, while foliar applications of Fe (as solutions of $FeSO_4$ or $EDTA{\cdot}Na_2Fe$ [0.5 $g\,L^{-1}$ Fe]) significantly increased the Cd concentration in brown rice by more than 35%.

However, research on the combined treatments of these low-cost measures is limited. Therefore, the present study was conducted to investigate the effects of quicklime combined with foliar applications of Zn/Fe on the accumulation of Cd in rice grain and rice straw.

2. Materials and methods

2.1. Site description

The field trial was located in Suxian County, Hunan Province (N, 25° 30′21″; E, 112° 53′55″). The experiment was conducted on an acidic Ultisol derived from quaternary red clay; the soil had been used for cultivating paddy rice for many years. Due to the large amounts of heavy metal-rich lignite used as fertilizer during 1970s and1980s, the soil has become contaminated with Cd (He et al., 2017). The mean annual temperature at the experimental site is 18.0 °C, and the average total annual precipitation is 1490 mm. Soil properties are presented in Table 1.

2.2. Experimental design and treatments

There were a total of 4 treatments: CK, control (no treatment); L, soil application of quicklime; LFe, soil application of quicklime and foliar application of $EDTA{\cdot}Na_2Fe$ solution at the panicle initiation stage 2 times; and LZn, soil application of quicklime and foliar application of $ZnSO_4$ solution at the panicle initiation stage 2 times. Due to previous studies conducted by our group and other researchers, the quicklime, $EDTA{\cdot}Na_2Fe$ and $ZnSO_4$ were applied at 900 $kg\,hm^{-2}$, 0.5 $g\,L^{-1}$ Fe and 0.3% (w/v), respectively (Huang et al., 2000; Shao et al., 2008; Saifullah et al., 2014). Before the plots were separated, the tested field was tilled to a depth of 15–20 cm. The plots were 6 m × 5 m in area and were randomly arranged in three blocks; each treatment was replicated three times. An 1.0 m ditch and a plastic film-covered ridge (0.3 m high and 0.3 m wide) were used to separate adjacent blocks and plots, respectively. After the plots were separated, the quicklime was hand-scattered over the soil surface and then mixed thoroughly via manual plowing to a depth of 10–15 cm. Five days later, a specific compound fertilizer (N:P:K = 16:8:16) for rice was applied at a rate of 900 $kg\,hm^{-2}$ as a base fertilizer. Two days later, 30-day-old rice seedlings were transplanted at a spacing of 0.20 × 0.25 m and at three seedlings per hole. The conventional *indica* cultivar Xiang Zaoxian 32 was used. Seven days after transplanting, urea was applied as a top-dressing fertilizer at a rate of 30 $kg\,N\,hm^{-2}$.

Table 1
Physical and chemical properties of the tested topsoil (0–20 cm).

Soil property	Unit	Value
pH	–	5.85
Soil organic carbon	$g\,kg^{-1}$	34.2
Total nitrogen	$g\,kg^{-1}$	2.68
Available phosphorus	$mg\,kg^{-1}$	26.9
Cation exchange capacity (CEC)	$cmol\,kg^{-1}$	15.7
Clay	%	48.9
Total Cd	$mg\,kg^{-1}$	1.46
Total Zn	$mg\,kg^{-1}$	200.79
Total Fe	$g\,kg^{-1}$	29.22
DTPA extractable Cd	$mg\,kg^{-1}$	0.65
DTPA extractable Zn	$mg\,kg^{-1}$	8.83
DTPA extractable Fe	$mg\,kg^{-1}$	264.89

2.3. Sampling and measurement

Before the lime was applied and after the rice was harvested, topsoil (0–20 cm) samples were collected from each plot. After they were air dried, the soil samples were sieved (< 2 mm and 0.15 mm), homogenized and preserved. Rice was harvested at the maturity stage, and samples of the rice grain and straw were collected. The samples were thoroughly rinsed with tap water followed by deionized water. The samples were then oven dried at 60 °C for 48 h, after which their water content was measured. During harvest, the fresh weights of the rice grain and straw of each plot were recorded for calculating the rice grain yield and straw biomass. All brown rice within the oven-dried grains was separated. In the end, the brown rice and rice straw were homogenized, sieved (< 1 mm) and save prior to analysis.

2.4. Determination of metals and soil properties

To determine the total Cd, Zn and Fe in the soil and plants, the soil samples and plant samples were digested in an open system using aqua regia-$HClO_4$ and HNO_3-$HClO_4$, respectively. The extractable Cd, Fe and Zn in the soils was measured in accordance with the method of Lindsay and Norvell (1978). The concentrations of Cd, Fe and Zn in solution were determined via inductively coupled plasma-optical emission spectrometry (ICP-OES 720; Varian, USA). Certified soil and a rice reference materials as well as three spikes and three blanks were used for quality control. The soil pH was directly determined with a pH meter (PHS-3C, Shanghai Dapu Instruments, P.R. China); the soil: water ratio used was 1:2.5 (m/v). The soil organic carbon (SOC) and TN contents were directly measured with a CN autoanalyzer (Vario MAX C/N, Germany). The Olsen-P, available K, CEC and clay content of the soils were analyzed as described by Lu (2000).

2.5. Data analysis

One-way ANOVA in conjunction with multiple comparisons by Duncan's test at $P < 0.05$ was used to compare the means among different treatments. All statistical analyses were completed using SPSS 11.5 (SPSS Inc. Chicago, USA).

3. Results

3.1. Soil pH and extractable Cd, Fe, and Zn in the soil

Soil pH of the CK treatment was 5.85 in average (Fig. 1). Compared with CK, treatments L, LFe and LZn increased the soil pH by 0.27, 0.63 and 0.32 units, respectively. While, a significant change was observed only in the LFe ($P < 0.05$). Compared with CK, treatments in which lime was applied with or without foliar application of Zn or Fe did not affect the DTPA-extractable Cd in the soils ($P > 0.05$). Compared with that in the soil of CK, the DTPA-extractable Fe and Zn in the soil of LFe