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Use of clay to remediate cadmium contaminated soil under different water management regimes

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ABSTRACT

We examined in situ remediation of sepiolite on cadmium-polluted soils with diverse water regimes, and several variables including brown rice Cd, exchangeable Cd, pH, and available Fe/P. pH, available Fe/P in soils increased gradually during continuous flooding, which contributed to Cd absorption on colloids. In control group (untreated soils), compared to conventional irrigation, brown rice Cd in continuous flooding reduced by 37.9%, and that in wetting irrigation increased by 31.0% ($p < 0.05$). In contrast to corresponding controls, brown rice Cd in sepiolite treated soils reduced by 44.4%, 34.5% and 36.8% under continuous flooding, conventional irrigation and wetting irrigation ($p < 0.05$), and exchangeable Cd in amended soils reduced by 27.5–49.0%, 14.3–40.5%, and 24.9–32.8% under three water management regimes ($p < 0.05$). Compared to corresponding controls, decreasing amplitudes of exchangeable Cd and brown rice Cd in sepiolite treated soils were higher in continuous flooding than in conventional irrigation and wetting irrigation. Continuous flooding management promoted soil Cd immobilization by sepiolite.

1. Introduction

The environmental toxicology of heavy metals contaminated soils have become a widespread concern, mainly due to anthropogenic sources including wastewater irrigation, atmospheric sedimentation, mine exploitation, application of chemical fertilizers and pesticides, and livestock manures. Most of all, the farmland soils polluted by heavy metals have already accounted for 20% of total agricultural acreage in China, and more than 40% of metal-contaminated soils were polluted by Cd (Wei and Chen, 2001). The excessive heavy metals deserted in soils would exceed the environmental capacity of retaining pollutants, resulting in heavy metals leaching into ground water or soil solution available for plant uptake. Heavy metals could also enter the human body through consumption of food plant grown in metal-polluted soils (Cambra et al., 1999; Dudka and Miller, 1999). Rice grains constitute an important part of the human diet since they contain carbohydrates, proteins, as well as vitamins, minerals, and trace elements. As a result, high accumulation of Cd in rice grains could pose a potential hazard to human health via food chain (Gupta and Gupta, 1998; Marisela and Camilo, 2007).

Recently, in situ stabilization of heavy metals in soils had gained prominence due to its high-efficiency, low-cost as well as its appearance as an alternative technology for a wide range of metal-polluted soils (Cao et al., 2008; Liang et al., 2011). A number of natural and synthetic materials, including phosphorus-containing materials (Fayiga and Ma, 2006; Cao et al., 2002), alkaline compounds (Brown et al., 2004; Garau et al., 2007; Lombi et al., 2002), organic matters (Crecchio et al., 2004), clay minerals (Li et al., 2009; Xu et al., 2010) and biosolids (Brown et al., 2004; Chen et al., 2007) have been adopted to stabilize heavy metals in soils. As everyone knows, sepiolite is natural hydrated magnesium silicate clay. There are gaps and inversions in the silica sheet generating tunnels and blocks. These tunnels are rich in H_2O and exchangeable ions. In the blocks, some of the corners are Si bound to hydroxyls, which are chief reactive centers for heavy metal polycation (Akçay, 2004; Tekin et al., 2006). Previous investigations have showed sepiolite was an effective amendment to reduce Cd uptake by rice plant grown in contaminated soils (Liang et al., 2011; Wang et al., 2011). What is more, rice plant has been shown to vary greatly among different water management in Cd accumulation from soils (Hu et al., 2010; Ji et al., 2007), and the oxidation/reduction of Fe oxides posed influences on colloids charges and Cd adsorption onto colloids in soils (Breennan and Lindsay, 1996; Favre et al., 2006).

However, use of clay combined with water management for Cd immobilization has rarely been reported. To illuminate the influences of water management on remediation of Cd-polluted paddy soils using sepiolite (Cd immobilization by sepiolite), under different water con-

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Table 1
The selected characteristics of soil and amendment.

Soil		Sepiolite	
Property	Value	Property	Value
pH	5.61	pH	10.32
Organic matter	1.98%	$CaCO_3$	65%
CEC	17.3 cmol/kg	$Mg_3Si_2(OH)_4O_5$	8%
Total P	0.51 g/kg	$Si_3O_6{\cdot}H_2O$	9%
Total Fe	19.1 g/kg	$CaMgSi_2O_6$	18%
Total Pb	50.8 mg/kg	Surface area	22.7 m^2/g
Total Cd	0.71 mg/kg	Average pore size	1.4 nm

dition, we examined the effects of sepiolite on exchangeable Cd in soils, biomass and Cd concentration of rice plant, with special emphasis on pH, redox potential, available Fe and P in soils.

2. Material and methods

2.1. Properties of soil and amendment

An in situ field-scale remediation was conducted in Guiyang located in the Hunan province, China (E: 112°13′26″ − 112°55′46″, N: 25°27′15″ − 26°13′30″). Guiyang was located at the upstream of Chong-ling Jiang, one of winding channels of Xiang Jiang. The local farmland was contaminated by Cd because of Pb and Zn smelting and mining.

Soil materials were sampled from rice fields at a depth of 0–20 cm in paddy soils. Soil samples that passed through a 20 mesh sieve were used for physical and chemical fraction analysis. Tested soils belonged to red earth with 40.1% clay, 10.3% silt and 49.6% sand, and the physical and chemical characteristics were listed in Table 1. Amendment materials (sepiolite), natural hydrated magnesium silicate clays, were obtained from a construction material company, and basic properties were shown in Table 1.

2.2. Experimental design

We made application of sepiolite to paddy soils at 1.50 kg m^{-2}, which was recommended by the same research group in remediation of Cd-polluted paddy soils with conventional irrigation condition (Liang et al., 2014). Sepiolite was mixed into topsoil (0–20 cm). Soil water management was carried out using following method, involving continuous flooding (5–7 cm surface water during the whole growth period of plant), conventional irrigation (moist soil surface during the late tillering state and grain filling stage, and 5–7 cm surface water during the other growth stages) and wetting irrigation (moist soil surface during the whole growth period of plant, 70% of field water-holding capacity). There were totally 6 experimental treatments (3 × 2) and 18 plots (each measuring 5 m × 6 m). Six treatments: CKys (control soils with continuous flooding), CKgs (control soils with conventional irrigation) and CKsr (control soils with wetting irrigation), and SPys (sepiolite treated soils with continuous flooding), SPgs (sepiolite treated soils with conventional irrigation) and SPsr (sepiolite treated soils with wetting irrigation).

The rice plants (TY-272, ordinary rice cultivar) transplanting were completed 30 days after sepiolite application, which was consistently with local conventional practices. A 250 g composite top soil sample was collected in each plot using five-point sampling and then air-dried for chemical analysis. After 90 days of growth, the rice plants were harvested and flushed with tap water, then rinsed 3 times with deionized water. The plants were divided into rice straw and brown rice, then dried to a constant weight at 65 °C in oven, plant samples were smashed with a stainless mill and passed through a 60 mesh sieve before physicochemical analysis.

2.3. Analytic methods

2.3.1. pH and redox potential

The first in situ determinations of pH and redox potential of topsoil of plots were implemented by automatic multi-function analyzer 10 days after rice plant transplanting, the next measurements were done at interval of 10 days (FJA-6), six-time determinations were totally done during the growing period of plant.

2.3.2. Cd chemical fractions

The sixth fresh soil sample collection from topsoil of plots was used to determine Cd chemical forms distribution. Sequential Extraction Procedure was conducted to evaluate Cd availability. The method partitioned metal into five operationally defined chemical fractions: exchangeable (1 M $MgCl_2$, agitation for 1 h), bound to carbonates (1 M CH_3COONa, plus CH_3COOH of pH 5, agitation for 5 h), bound to Fe/Mn oxides (0.04 M $NH_2OH{\cdot}HCl$ in 25% CH_3COOH, agitation for 6 h at temperature of 96 ± 3 °C), bound to organic matters (0.02 M HNO_3 and 30% H_2O_2, agitation for 5 h at temperature of 85 ± 2 °C) and residual Cd (Wang et al., 2011).

2.3.3. Total Cd

Three rice plant specimens, including rice straw and brown rice, were collected randomly from each plot during the harvesting and brown rice grains were obtained with a thresher. A 0.50 g sample of plant powder was digested using a 10 ml of HNO_3 solution, and the concentrations of Cd in solutions were determined by inductively coupled plasma mass spectrometer (ICP-MS, American Thermofisher Company). Bush leaf (GBW07603, China) materials, as certified reference materials, were used to evaluate the accuracy of digestion procedure and subsequent analysis, the accuracy obtained using reference material was 3.1% (RSD).

2.3.4. Available Fe/P

The in situ sampling was implemented to conduct available Fe/P determinations of topsoil of plots. The first sampling of soil material was done 10 days after rice plant transplanting, the next sampling was done at interval of 10 days.

Fe testing: 25.0 g of fresh soil sample that passed through a 20 mesh sieve and 50 ml of DTPA solution were put in plastic bottle respectively, then the mixture was agitated for 2 h at 25 °C, and the Fe in soil extract was determined by atomic absorption spectrophotometer and calculated as available Fe in soil. P testing: 25.0 g of fresh soil sample passed through a 20 mesh sieve was put in plastic bottle, and 50 ml of $NaHCO_3$ solution (pH 8.5, 0.5 M) was put in the bottle, then the mixture was agitated for 30 min at 25 °C and filtered, and 10 ml of filtrate was blended with 5 ml of visualization reagent for 30 min. The phosphorus in extract was determined by Mo-Sb colorimetric method and calculated as available P in soil.

2.4. Statistical analysis

All treatments in the investigation were replicated three times. All data were represented as means ± standard deviations. Analysis of variance was implemented with the software SAS 9.2. When significant differences were observed between treatments, multiple comparison were made by LSD test ($p < 0.05$).

3. Results

3.1. Brown rice production and plant Cd

As shown in Fig. 1a, in control soils, in contrast to conventional irrigation, brown rice production reduced by 6.2% in continuous flooding, and 13.6% in wetting irrigation ($p < 0.05$). The brown rice productions were not affected by sepiolite application.