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Research article

## Immobilization remediation of Cd-polluted soil with different water condition

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## ABSTRACT

To demonstrate effects of water management on soil Cd immobilization using palygorskite, the investigation evaluated impacts of palygorskite on uptake of Cd present in soils with different water condition by rice plant. Pot experiment results showed that, pH, available Fe and P in untreated soils were higher in continuous flooding than in traditional irrigation and wetting irrigation, which were reasons for lower soil exchangeable Cd and plant Cd in continuous flooding. In control group (untreated soils), compared to traditional irrigation, continuous flooding reduced brown rice Cd by 37.9%, that in wetting irrigation increased by 31.0%. At palygorskite concentrations of 5 g kg<sup>-1</sup>, 10 g kg<sup>-1</sup> and 15 g kg<sup>-1</sup>, brown rice Cd reduced by 16.7%, 44.4% and 55.6% under continuous flooding, 13.8%, 34.5% and 44.8% under traditional irrigation, 13.1%, 36.8% and 47.3% under wetting irrigation ( $p < 0.05$ ). At the same palygorskite addition, decreasing amplitude of brown rice Cd was higher in continuous flooding than in traditional irrigation and wetting irrigation. Competition for adsorption sites in root coating between Cd<sup>2+</sup> and Fe<sup>2+</sup> was another factor governing plant Cd. In control group, compared to traditional irrigation, root coating Fe(II) increased by 124.5% and root coating Cd reduced by 17.6% upon continuous flooding ( $p < 0.05$ ). In conclusion, palygorskite addition combined with continuous flooding was an efficacious technique to stabilize Cd in paddy soils.

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### 1. Introduction

China has undergone rapid industrialization and urbanization over the last two decades. As a result, environmental contamination involving heavy metals has become a widespread concern that affects public health. The farmlands polluted by heavy metals have already accounted for 16.7% of crop acreage in China, and more than 40% of metals-contaminated soils were contaminated by cadmium (Song et al., 2013). Cadmium is a non-essential metal element that is believed to cause damage even at very low concentrations and can be taken up by crops easily (Wagner, 1993). The rice plants, one of the main food crops in China, were capable of accumulating relatively high levels of Cd from contaminated soils. As a consequence, high accumulation of Cd in rice grains would pose a potential hazard to human health via food chain (Alloway, 1995; Marisela and Camilo, 2007).

In recent years, in situ stabilization of heavy metals in soils has

gained prominence due to its high-efficiency, low-cost as well as its appearance as an alternative technology for a wide range of contaminated soils (Cao et al., 2002, 2008). The frequently-used amendments contain alkaline compounds (Brown et al., 2004; Gray et al., 2006; Neumann and Zurnieden, 2001), phosphorus-containing materials (Mirelzyk and Fernandez-Cirelli, 2008; Yang and Mosby, 2006), clay minerals (Sun et al., 2012, 2013; Xu et al., 2010) and organic matters etc. (Crecchio et al., 2004). Among them, the clay minerals, such as sepiolite, vermiculite and palygorskite, which are particularly abundant and inexpensive, have a high cation exchange capacity and high specific surface area associated with their small particle sizes. Such properties have made these materials preferential amendments for remediation of metal-polluted soils. The investigations have shown that palygorskite was an effective amendment to reduce Cd in polluted soils uptake by plant (Liang et al., 2011; Wang et al., 2011).

Then again, phytoavailability of Cd in acid soils has been proved to be marked distinctions among different water management (Hu et al., 2010), and the oxidation and reduction of various Fe oxides affected the Cd absorption onto colloids and Cd bioavailability in

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soils (Favre et al., 2006).

However, the technologies of palygorskite application combined with water management, used for metal-contaminated soils remediation, have not been reported so far. In the investigation, under different water condition, influences of palygorskite on exchangeable Cd in soils, biomasses and Cd concentrations of rice plant were discussed. Meanwhile, several factors determining Cd availability, including pH, available Fe and available P, were surveyed.

## 2. Materials and methods

### 2.1. Palygorskite properties

The palygorskite materials, as a naturally occurring clay minerals with 64.4% SiO<sub>2</sub>, 20.5% MgO, 10.4% Al<sub>2</sub>O<sub>3</sub>, 1.5% Na<sub>2</sub>O and 1.2% CaO, were supplied by a material manufacturer, it had a good cation exchange capacity (CEC = 4.53 meq g<sup>-1</sup>) and a high pH value at a point of zero charge (pH = 9.53).

### 2.2. Soil characterization and plant culture

The soil used in pot experiment was topsoil (0–20 cm) collected from rice field in Guiyang located in Hunan province, China. Guiyang was located at the upstream of Chong-ling Jiang, one of winding channels of Xiang Jiang. The local farmland was polluted by Cd due to Pb and Zn smelting and mining. Soil materials having been passed through a 20 mesh sieve were prepared for physicochemical property analysis. Soils examined in this study were classified as red earth, and Table 1 reported its selected properties.

The investigation contained two factors, namely water management and palygorskite addition. Water management was carried out using weighing method, involving continuous flooding (3–4 cm surface water during the whole growth period of plant), traditional irrigation (moist soil surface during the late tillering state and grain filling stage, and 3–4 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). 7.5 kg of soil sample was ground, passed through a 4 mm sieve, and put in each plastic pot, and palygorskite was blended into soils at concentrations of 0 g kg<sup>-1</sup>, 5 g kg<sup>-1</sup>, 10 g kg<sup>-1</sup> and 15 g kg<sup>-1</sup>. There were totally 12 experimental treatments (3 × 4) and 36 plastic pots (3 duplications for each treatment). CK, BC1, BC2 and BC3 meant palygorskite treated soils with applications of 0 g kg<sup>-1</sup>, 5 g kg<sup>-1</sup>, 10 g kg<sup>-1</sup> and 15 g kg<sup>-1</sup>, respectively.

Soil material was left to equilibrate for 45 d at level of 70% of field water holding capacity, then three rice seedlings were planted in each plastic pot. After 120 days of growth, rice plants (JD-78, ordinary rice cultivar) were harvested and flushed with tap water, then rinsed 3 times with deionized water. The plants were divided

into root, 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 0.25 mm sieve before physicochemical analysis.

### 2.3. Analytic methods

#### 2.3.1. pH and exchangeable Cd

The in situ determinations of pH of soils in plastic pots were done using automatic multi-function pH analyzer (FJA-6) before harvest of rice plant. 2.0 g of fresh soil sample and 10 ml of 1.0 mol L<sup>-1</sup> MgCl<sub>2</sub> solution were put in plastic bottle respectively, then the mixture was agitated for 1 h at 25 °C, and the Cd in soil extract was determined by atomic absorption spectrophotometer and calculated as exchangeable Cd in soils (Tessier et al., 1979).

#### 2.3.2. Total Cd

The plant and soil samples were treated with mixtures of HNO<sub>3</sub>–HClO<sub>4</sub> and HNO<sub>3</sub>–HF–HClO<sub>4</sub>, respectively. The resulting solutions were filtered with paper filter and diluted to 100 ml with high purity water. The solutions were employed for the ACP-IES analysis. Bush leaf materials, as reference materials, were applied to verify the precision of digestion and analysis.

#### 2.3.3. Available Fe/P

The in situ sampling was used to conduct the available Fe/P determination of soils in plastic pots before harvest of rice plant. Fe determination: 25.0 g of fresh soil sample 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 determination: 25.0 g of fresh soil sample that passed through a 20 mesh sieve was put in plastic bottle, and 50 ml of NaHCO<sub>3</sub> solution (pH 8.5, 0.5 mol L<sup>-1</sup>) 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 soils.

#### 2.3.4. Fe(II)/Cd in root coating

The fresh roots were firstly treated with 0.100 mol L<sup>-1</sup> Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution, then a filtration step was followed, lastly the leachates were collected and Fe(II) in leachates were determined by atomic emission spectroscopy to calculated as Fe(II) in root coating, and the roots were sequentially treated using DCB (0.030 mol L<sup>-1</sup> Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O, 0.125 mol L<sup>-1</sup> NaHCO<sub>3</sub> and 0.600 g of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) solution, then above-mentioned two leachates were collected, and sum of Cd in above-mentioned two leachates were counted as Cd in root coating (Lu, 2000).

### 2.4. Statistical analysis

Each treatment was performed in triplicate in the experiment. The means, standard deviations and analysis of variance were performed with the software SAS (version 9.1). When significant differences were observed between treatments, multiple comparison were made by LSD test ( $p < 0.05$ ).

## 3. Results and discussion

### 3.1. Biomass and Cd concentration of plant

The plant biomasses, as shown in Fig. 1, followed the sequence brown rice < rice straw. In control soils, in comparison to traditional irrigation, brown rice biomasses reduced by 11.5% and 23.7%,

**Table 1**  
The general physicochemical characteristics of tested soils.

Properties	Value
pH	5.61
Organic matter (%)	1.98
CEC (cmol kg <sup>-1</sup> )	17.3
Total N (g kg <sup>-1</sup> )	1.03
Total P (g kg <sup>-1</sup> )	0.51
Total Fe (g kg <sup>-1</sup> )	19.1
Total Cd (mg kg <sup>-1</sup> )	0.71
Particle size distribution (%)	
Clay	40.1
Silt	10.3
Sand	49.6

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