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Ca-containing amendments to reduce the absorption and translocation of Pb in rice plants

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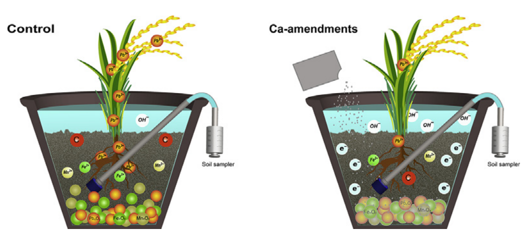
HIGHLIGHTS

- Ca-amendments significantly reduced Pb in grains of two indica rice cultivars.
- Reduced Fe/Mn oxide dissolution was the major mechanism for Pb reduction.
- Higher pH induced by the amendments also contributed to the Pb reduction.
- Lower Eh induced by the amendments played a role in Pb reduction.

GRAPHICAL ABSTRACT



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ABSTRACT

The influence of three Ca-containing amendments (dolomite, slaked lime, and limestone) on soil water soluble Pb (Pb-w) levels, Pb accumulation by two rice plants (TJ-8, japonica and II-3301, indica), and the factors affecting Pb-w were investigated. Pot experiment was performed under waterlogged conditions using Pb-contaminated soil collected from an agricultural field near a mine. It was found that the soil amendments significantly reduced Pb content in the rice plants in the order dolomite > slaked lime > limestone, irrespective of rice cultivar. The Pb content of brown rice with the added soil amendments was lower than that of the recommended limit (0.2 mg kg^{-1}, GB2762-2017) except for cultivar II-3301 with slaked lime. There was a significant positive correlation between the Pb content of the roots, stems, leaves, and grains and the soil Pb-w levels. The amendments reduced soil Eh, Fe, and Mn concentrations in the pore water and increased soil pH. The total organic carbon (TOC) in the pore water significantly decreased for II-3301 but not for TJ-8 at the ripening stage after addition of the amendments. Among soil Eh, pH, TOC, Fe, and Mn in the pore water, Fe and Mn were the most influential in lowering soil Pb-w levels. The amendments inhibited the formation of iron plaques on the root surface and reduced Pb adsorption. The Pb content of the roots was positively correlated with that in iron plaque. These findings are significant as they imply that the application of Ca-containing amendments in Pb-contaminated paddy soils near mines is an effective approach for *in situ* immobilization of Pb and reduction in Pb levels in the edible parts of crops.

1. Introduction

Lead (Pb) is a highly toxic element and widespread environmental pollutant. In recent years, an increasing number of reports have shown that agricultural soils are suffering from Pb pollution due to human activities (Li et al. 2000). For example, the average Pb concentration was 1486 mg kg^{-1} in paddy soils near a lead-zinc mine in Lechang of Guangdong province, China (Yang et al. 2004). In another case, Pb levels were 144,573 ± 49,812 and 38,521 ± 28,581 mg kg^{-1} in soils around traditional artisanal zinc smelting operations in Shuitang and Hejiachong villages of Magu Town, in the Guizhou province of China (H et al., 2013). Pb levels also reached 1602 mg kg^{-1} in paddy soil near a smelter in Youxi county, Fujian Province, China (Li et al. 2016a). These studies highlight the problem of Pb contamination of soils near mines, whose levels significantly exceed the Chinese limit

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for acidic agricultural soil (250 mg kg^{-1}, pH < 6.5, GB15618-1995). Pb uptake by plants and translocation to edible parts presents significant concern for people consuming those crops. Rice is a staple food crop in Southern China and is also cultivated worldwide in mining areas. The consumption of rice represents a dominant route of Pb exposure for Asian populations. Indeed, some studies have shown that Pb levels in rice grains were as high as 1136 μg kg^{-1} in parts of Southern China, nearly 5.7 times higher than the Chinese national limit for Pb in rice (200 μg kg^{-1}, GB2762-2017) (Cheng et al. 2006). This implies that farmland remediation is of utmost importance to limit the risks to public health posed by Pb exposure (Singh et al. 2010; Williams et al. 2009).

Several techniques including soil washing (Sierra et al. 2010; Yoo et al. 2017) and phytoremediation (Huang et al. 1997; Salido et al. 2003) have been used to remediate the soils polluted by Pb. Immobilization of Pb in the soil is an effective approach to mitigate Pb uptake by plants (Ashrafi et al. 2015; He et al. 2013). The aim of *in situ* Pb immobilization in the soil is to achieve a redistribution of Pb to less mobile soil fractions (Chen and Zhu 2006; Cui et al. 2010). Ca-containing materials, such as lime and dolomite, are low-cost, practical and have been widely used as amendments to remediate heavy metal polluted soil (Ahmed et al. 2008; Vondrackova et al. 2013; Tan et al., 2011; Wu et al., 2006). It was previously reported that limestone and slaked lime could reduce Pb mobility and uptake by plants through adsorption, complexation, and precipitation mechanisms (Han et al., 2013; Vondrackova et al. 2013). Dolomite has been useful in ameliorating magnesium deficient soils in Southern China (Ahmed et al. 2008). Some studies have also found that dolomite application improved the growth of plants, increased their yield, and significantly decreased the accumulation of heavy metals (Ahmed et al. 2008; Wu et al., 2006). It is commonly believed that the reduction in the bioavailability of heavy metals in soils is the dominant mechanism by which these alkaline immobilization agents reduce the accumulation of Pb by plants. Although the water soluble Pb levels (Pb-w) in soil were relatively low, they represent an important source for Pb uptake in plants (Concas et al. 2015). To a certain extent, soil amendments could inhibit the translocation of Pb to the edible parts by reducing Pb-w levels. However, the mechanism by which Ca-containing amendments affect the Pb-w remains poorly understood. Moreover, further study is required to determine whether Ca-containing amendments can reduce the accumulation of Pb in plant tissues, especially in grains, by affecting the translocation and distribution of Pb in rice. Therefore, it is necessary to analyze the translocation and redistribution of Pb in soil-rice systems to gain a more complete understanding of the immobilization effects of Ca-containing amendments. To achieve these objectives, pot experiments, *i.e.*, rice cultivation in lead-zinc (Pb-Zn) mining-contaminated soils with the addition of three Ca-containing (limestone, slaked lime, and dolomite) amendments, were conducted to measure changes in Pb levels in the pore water over the course of rice growth. The pH, Eh, Fe, Mn, and total organic carbon (TOC) were measured to explore the many factors affecting soil Pb-w levels. Meanwhile, the content of Pb in the plant tissues was analyzed to understand effects of the Ca-containing amendments on the translocation and redistribution of Pb in rice.

2. Materials and methods

2.1. Soil collection and experimental materials

The soils used in this experiment were taken from Pb-polluted paddy fields near a Pb-Zn mining area in Datian County, Fujian Province, China. The soil was air-dried and ground to pass a 2 cm sieve. The physiochemical properties (pH, organic matter, cation exchange capacity, texture, total Pb, and available Pb) of the soil are listed in Table S1. The total Pb in the soil was 450 mg kg^{-1} and the $CaCl_2$-extracted Pb was determined to be 177.5 mg kg^{-1}, indicating that the soil was seriously polluted with Pb. Three Ca-containing materials (dolomite powder, slaked lime powder, and limestone powder) were purchased from the Xinchuan mineral processing plant, Hebei province, China. The pH of the dolomite, slaked lime, and lime (materials:water = 1:2.5, w/w) was 10.4, 12.8 and 12.7, respectively. Differences among rice cultivars in the translocation of Pb in rice plants were considered significant at a p value < 0.05 (Lai et al. 2017; Liu et al. 2013). Taijing 8 (TJ-8, Japonica) and II-3301 (II-3301, Hybrid Indica) were the cultivars used in this study.

2.2. Pot experiment and sample collection

The pot experiment was performed at 25–28 °C in a greenhouse in Fuzhou, China. First, 7.5 kg of paddy soil was weighted into the pot (diameter and height of 25 cm) and the soil was supplemented with $CO(NH_2)_2$ (2.1 g), $NH_4H_2PO_4$ (1.2 g), and K_2SO_4 (2.1 g) as basal fertilizers for rice cultivation. Eight treatment groups were prepared: TJ-8 without amendments (TJ-CK), TJ-8 with dolomite (TJ-D), TJ-8 with limestone (TJ-L), TJ-8 with slaked lime (TJ-SL); II-3301 without amendments (II-CK), II-3301 with dolomite (II-D), II-3301 with limestone (II-L), and II-3301 with slaked lime (II-SL). The doses of dolomite, limestone, and slaked lime were 2.7, 2.7, and 2.0 g kg^{-1}, respectively. The soil was thoroughly mixed with the amendments, flooded, and allowed to equilibrate for 30 days. Each treatment group had three replicates. Before the transplanting the rice seedlings, Fourrhizon samplers (Rhizosphere Research Products, Wageningen, Holland) were inserted vertically into the soil to collect the pore water. The homogenous seedlings (TJ-8 and II-3301 three seedlings per pot) were transplanted into the Pb-contaminated soils after 23 days of hydroponic culture. The flooding conditions (2 cm of distilled water) were maintained and the pore water was collected every 15 days during rice cultivation. The pH and Eh were measured immediately in the pore water and it was then acidified with HNO_3 (GR) and passed through a 0.45 μm nylon filter prior to further analysis. After the rice plants reached maturity, they were harvested and washed thoroughly with deionized water. Each plant was then separated into root, stem, leaf, and grain. The rhizosphere was sampled by shaking the roots.

2.3. Iron plaque extraction

The dithionite-citrate-bicarbonate (DCB) method was used to extract the iron plaque on the root surface (Li et al. 2017). Briefly, the thoroughly rinsed roots were immersed in 50 mL of DCB extraction buffer containing 0.5 g of sodium dithionite ($Na_2S_2O_4$), 0.03 mol L^{-1} sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), and 0.125 mol L^{-1} sodium bicarbonate ($NaHCO_3$)) at 25 °C. After 1 h, the roots were washed three times with deionized water in a total volume of 100 mL. All samples (roots, stems, leaves, grains, and rhizosphere) were dried at 70 °C and their dry weight was recorded. The samples were then ground into fine powders, and kept at −20 °C until needed for further analysis. The rhizosphere was ground through 100-mesh sieves prior to further analysis.

2.4. Analytical methods

The soil samples (100 mg) were digested with HCl (GR), HNO_3 (GR), $HClO_4$ (GR), and HF (GR). The plant samples (100 mg) were digested with HNO_3 (GR) and H_2O_2 (GR). The Pb, Fe, Mn contents were measured using inductively coupled plasma mass spectrometry (ICP-MS, NexION300X, Perkin Elmer, USA). The pH and Eh of the samples were measured using HQ30d multi-parameter meters (HACH, USA). The TOC of the samples was determined using an elemental analyzer (Vario Max Cube, Elementar). The soil texture was measured by the pipette method after hydrogen peroxide treatments. The recovery of Pb from the rice grain (GBW-10023) and soil (GBW-07402) was 95–107%.