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Effects of soil acidification and liming on the phytoavailability of cadmium in paddy soils of central subtropical China[☆]

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ABSTRACT

Intensive and paired soil and rice grain survey and multiple-field liming experiments were conducted to assess soil acidification in the past 30 years, quantify the relationships of Cd phytoavailability with soil acidity, and determine efficacies of liming on soil acidity and Cd phytoavailability in paddy soils of central subtropical China at a regional scale. Soil pH, total and extractable Cd (Cd_{tot} and Cd_{ext}), rice grain Cd were determined, and all measured data were analyzed separately in groups of 0.1 pH units intervals. Paddy soil pH averagely declined at 0.031 unit yr^{-1} between 1980s and 2014 ($P < 0.01$). Piecewise means of log Cd transfer ratio kept around −0.062 between soil pH 4.0 and 5.5 and around −1.31 between pH 6.9 and 7.3, whereas linearly decreased by a factor of 0.76 with pH 5.5–6.9, and by a factor of 1.38 with pH 7.3–8.2 ($P < 0.01$), respectively. Similar responses to soil pH were observed for soil Cd_{ext} to Cd_{tot} ratio. However, the former exhibited a lag effect to soil acidification in the acidic soils and a leading effect in alkaline soils. Liming increased soil pH by 0.50 units, and decreased rice grain Cd by 35.3% and log Cd transfer ratio by a factor of 0.76 ($P < 0.01$). The piecewise relationship based on the survey precisely predicted the changes in Cd transfer ratio across the multiple-field liming experiments. In conclusion, soil acidification occurred and accelerated in the past 30 years, and piecewise-linearly increased Cd phytoavailability of paddy soils in central subtropical China. Mitigating soil acidification, i.e. liming, should be preferentially implemented to minimize Cd phytoavailability.

1. Introduction

Soil acidification has recently received increasing attention because of its essential impacts on the quality of soil environment, the phytoavailability of soil heavy metals, and food security and human health (McBride, 2002; Godfray et al., 2010; Guo et al., 2010). Rice (*Oryza sativa* L.) is the staple crop in Asia, e.g. China, India, Japan and Korea (Zhang et al., 2005). Unfortunately, soil Cd contamination occurs widely in such countries, especially in paddy fields of subtropical China, posing a major threat to the food safety (Zhao et al., 2010; Zhang, 2015; Zhang et al., 2015). It is widely reported that soil acidification may increase the phytoavailability of Cd in the soil and the accumulation Cd in rice grain (Zhao et al., 2010; Zeng et al., 2011; Wang et al., 2015a). However, the impacts of soil acidification on Cd phytoavailability of paddy soils are still unclear, particularly the quantitative effects at a regional scale, although they may provide valuable information for the minimization of rice grain Cd.

Soil acidification, affecting approximately 30% of the total ice-free land area, is a major problem for agricultural sustainability throughout much of the world (Sumner and Noble, 2003). Soils acidify slowly under natural conditions, mainly related to mineral weathering, soil parent materials and rainfall (Ulrich and Sumner, 1991). However, soil acidification may be accelerated by the high levels of N fertilization, the enhanced uptake and removal of base cations by crops, the local acid rain and industrial climatic conditions (Larssen and Carmichael, 2000; Zhang et al., 2009; Guo et al., 2010).

Soil acidification, normally indicated by soil pH decline, strongly increases the phytoavailability of soil heavy metals and the risks of grain heavy metals contamination (McBride, 2002; Zhao et al., 2010; Zeng et al., 2011; Wang et al., 2015a). Soil pH is the single

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factor most consistently cited as the parameter controlling the speciation, solubility, mobility and phytoavailability of Cd in soils (Christensen, 1984; McBride, 2002; Zhao et al., 2010). For example, Cd adsorptive capacity of loamy sand and sandy loam soils was reported to decrease by a factor of 3.0 for one pH unit decline between pH 7.7 and 4.0 (Christensen, 1984). More than 100-year experiments at Rothamsted Experimental Station exhibited that, soil acidification to pH 4 mobilized 60%–90% of total soil Cd (Blake and Goulding, 2002). Extractable Cd was reported to increase by factors of 0.35–0.37 with one pH unit decline in acidic (pH 4.7–6.7) paddy soils of subtropical China (Rao et al., 2013). However, results from paddy soil survey in Western Thailand showed that change in soil extractable Cd was closely related to soil pH, but their relationship was nonlinear between pH 5.5 and 7.7 (Simmons et al., 2008). Similar results were reported in the Yangtze River delta area (Wang et al., 2015a). Recent studies also reported that influence mechanisms of soil acidity on soil Cd phytoavailability were disparate in different soil acid-base conditions (Meers et al., 2007; Wang et al., 2009). So far, little information is available on quantitative impacts of soil acidification on Cd phytoavailability of paddy soils at a regional scale, since previous studies were always conducted at plots or across small areas with narrow ranges of pH or Cd contents.

Liming is a popular practice in mitigating soil acidification, and reducing the soil heavy metals availability and their uptakes by crops (Bolan et al., 2003a). Liming may increase soil pH, and then immobilizes heavy metals by increasing soil adsorption and enhancing the transform from soluble metals to residuals (Zeng et al., 2011; Wang et al., 2015b). It also increases soil Ca^{2+} and cation exchange capacity (CEC), and consequently promotes metal-holding capacity of soil and the competition with Cd^{2+} on root surface (Bolan et al., 2003b). In some cases, however, liming could not decrease the uptake of Cd due to the high buffer capacity of certain soil (Tiller et al., 1997). There is an urgent need to quantify impacts of liming on soil acidity and Cd phytoavailability at a regional scale, because it is relevant for mitigating heavy metals contamination in food crops.

The subtropical China is the dominant rice cropping region, playing a role in national grain production (Zhang et al., 2015). However, this region is facing with the increasing threats of soil acidification and heavy metals pollution over the last three decades coinciding with rapid industrialization and urbanization (Zhao et al., 2015). Topsoil pH of paddy fields averagely declined 0.13 units between 1980s and 2000s (Guo et al., 2010), and more than 30% paddy soils were polluted by heavy metals in this region (Zhang et al., 2015). Recently, paddy Cd contamination has been more sensitive to the government and a growing concern to the public (Greenpeace East Asia, 2014; Zhang, 2015; Zhao et al., 2015). Elevated phytoavailability of soil Cd has been assumed as a key cause, and minimizing the transfer of Cd from soil to rice grain is a top priority (Zhao et al., 2015). These facts indicate an urgent need to unveil and quantify the relationships between soil acidification and soil heavy metal phytoavailability at a regional scale.

Regional paired soil and rice grain survey and multiple-field liming experiments were conducted across the paddy soils of central subtropical China. The present study aimed to: 1) assess the soil acidification in the past 30 years, 2) to quantify the relationships of Cd phytoavailability with soil acidity, and 3) to determine the efficacies of liming on soil acidity and Cd phytoavailability in paddy soils of central subtropical China.

2. Materials and methods

2.1. Study area

This study was conducted in Changsha, Zhuzhou and Xiangtan cities, Hunan Province (26°03′–28°40′ N, 111°53′–114°07′ E), the central subtropical China (Fig. 1). The study region covers 28,096 km^2, has a subtropical monsoon climate, with an annual mean temperature of 16.8–17.9 °C and precipitation of 1260–1550 mm. Both temperature and precipitation increased gradually from the northern to the southern. Paddy field is the major cropland, accounting for more than 75% of total cropland in this region. The soil of the paddy fields is classified as Anthrosols according to the USDA classification, mainly developed from Quaternary earth clay, granite, sandy shale, slate, and their alluvial deposits. The paddy fields have been cultivated for double rice production for centuries. Usually, the early rice is transplanted in middle March and harvested in late June, while the late rice is transplanted in early July and harvested in the late October. The paddy fields are mainly irrigated from Hsiang River or their adjacent reservoirs. Liming was commonly conducted at a rate of 1250–1500 kg ha^{-1} yr^{-1} between the late 1970s and the early 1980s (He, 1992). However, liming has declined greatly since the middle 1980s, because it is a labor-intensive without early and obvious economic benefit.

2.2. Multiple-field liming experiments

Liming experiments were conducted in 33 sites of the moderate acidic paddy soils across the study region (Fig. 1). For each experiment site, paired treatments, control (CK) and liming, were applied in triplicate. Each of the paired treatments was arranged in a parcel of paddy field (0.1–0.2 ha), and separated by a 0.3 m border. There was a 10-m distance between the parcels of paddy field. For the liming treatment, burnt lime (about 75% CaO, <0.01 mm) was applied at a rate of 1500 kg ha^{-1} yr^{-1} before soil tillage. Soil total Cd ranged from 0.12 to 1.25 mg kg^{-1}, while soil pH ranged from 5.0 to 6.8, representing the main paddy soils in this region. Rice crop cultivation and field management, including pest and weed control, among others, were performed according to local farming practices.

2.3. Survey and sampling

For the paddy lands of 400,000 ha (excluding the paddy lands adjacent to mining or industrial areas) in this region, a total of 39,642 sampling points were set at every 10 ha land in October 2014 (Fig. 1). Each of sampling point was approximately located at the central parcel (0.1–0.2 ha) of every 10 ha paddy field. A GPS (Global Positioning System) was used to locate the sampling points. At each sampling point, 500 g of soil sample was bulked from top 20 cm soil layer, and 500 g of rice grain sample was collected synchronously at physiological maturity of the late rice crop prior to harvest (late October). For each treatment of multiple-field liming experiments, soil and rice were sampled likewise.

Each soil sample was air-dried, homogenized thoroughly, and ground to <2 mm and 0.149 mm to determine pH, extractable Cd (Cd_{ext}), and total Cd (Cd_{tot}). Each rice grain sample (brown rice, unpolished) was oven-dried at 60 °C for 48 h, ground to 0.149 mm, and homogenized thoroughly to measure total Cd. To assess changes in topsoil pH, additional data from 4455 sampling sites of paddy soils in the study region were collected from the Second National Soil Survey in the early 1980s.

2.4. Soil and rice samples analyses

Soil pH was measured in distilled water at a soil-solution ratio of 1:2.5 (w/v) using a Mettler Toledo 320 pH meter (Mettler-Toledo Instruments Ltd., China). Soil Cd_{ext} was determined by tumbling soils at 30 rpm for 2 h in 0.005 mol L^{-1} DTPA (Diethylenetriaminepentacetic Acid), 0.1 mol L^{-1} triethanolamine, and