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Research article

# Effects of continuous fertilization on bioavailability and fractionation of cadmium in soil and its uptake by rice (*Oryza sativa* L.)

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A four-year field trial was conducted in a rice paddy in southern China to determine the effects of continuous phosphate fertilizer, pig manure, chicken manure, and sewage sludge application on soil Cd accumulation in soil and Cd uptake by rice. The results showed that continuous application of fertilizers with higher Cd levels caused Cd to accumulate and redistribute in various soil fractions. In turn, these effects influenced Cd bioavailability in rice plants. After four years of phosphate fertilizer, pig manure, chicken manure, and sewage sludge application, the annual soil Cd accumulation rates were 0.007–0.032 mg $kg^{-1}$, 0.005–0.022 mg $kg^{-1}$, 0.002–0.013 mg $kg^{-1}$, and 0.032–0.087 mg $kg^{-1}$, respectively. Relative to the control, the pig- and chicken manure treatments significantly increased soil pH and reduced DTPA-extractable Cd (DTPA-Cd) and the exchangeable Cd fraction (Exc-Cd). In contrast, sewage sludge application significantly increased DTPA-Cd and Cd in all soil fractions. Phosphate fertilization had no significant effect on soil pH, DTPA-Cd, or Exc-Cd. Pearson's correlation coefficients showed that the rice grain Cd levels varied directly with DTPA-Cd, and Exc-Cd but inversely with soil pH. Pig- or chicken manure decreased rice grain Cd content, but sewage sludge increased both soil Cd availability and rice grain Cd uptake. Application of phosphate fertilizer had no significant effect on rice grain Cd content. The continuous use of organic- or phosphate fertilizer with elevated Cd content at high application rates may induce soil Cd accumulation and influence rice grain Cd accumulation.



## 1. Introduction

As a consequence of industrialization and urbanization over the past three decades, China is facing the threat of heavy metal soil pollution. According to the National Soil Contamination Survey proposed by the Ministries of Environmental Protection (MEP) and Land and Resources (MLR) of the People's Republic of China, 16.1% of the surveyed sites are contaminated with inorganic- and organic pollutants (MEP, 2014). Approximately 82.4% of the soils classified as contaminated are polluted by heavy metals and semi-metals (Cd, As, Hg, Cu, Pb, Cr, Zn, and Ni) (MEP, 2014). Heavy metal contamination of agricultural soils lowers yield, reduces crop quality, and increases human dietary heavy metal intake via the soil-plant-food chain (Peralta-Videa et al., 2009). Cadmium (Cd) is considered to be the most toxic heavy metal to humans and ranks first in the proportion of soil samples (7.0%) exceeding the MEP limit (Nakadaira and Nishi, 2003; Yang et al., 2004; Andresen and Küpper, 2013).

Rice (*Oryza sativa*) is the dietary staple for ≥60% of the Chinese population and contributes to ~40% of the domestic grain yield (Yang et al., 2006). Rice has a greater potential for Cd uptake and accumulation than other cereals (Chaney et al., 2004). It is the major source of dietary Cd intake in human populations subsisting on rice (Grant et al., 2008; Arao et al., 2010; Meharg et al., 2013). Heavy metal soil pollution severely threatens rice quality. Cd contamination of paddy rice has been identified in many regions (Zhen et al., 2008; Zhang et al., 2009; Williams et al., 2009; Qian et al., 2010; Du et al., 2013; Fang et al., 2014). Rice grown in areas

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impacted by mining and other industries has often failed to meet the Cd limit food standard in certain parts of southern China (Williams et al., 2009; Du et al., 2013). Market basket surveys reported that in recent years, 2–13% of the rice grain samples exceeded the limit, causing widespread public concern (Zhen et al., 2008; Qian et al., 2010; Fang et al., 2014). As a result, the residents of the rice farming areas of southern China may have relatively higher dietary Cd intakes than the general population. Therefore, effective methods are needed to prevent the production of Cd-contaminated rice and reduce the potential health risk for those people using rice as a dietary staple.

The first step in preventing the contamination of rice with heavy metals is to identify and block the main pollution sources in soil-rice systems. Atmospheric deposition and livestock manure, sewage sludge, fertilizers, and other soil amendments all contribute to the accumulation of Cd in agricultural soils (Chen et al., 2007; Grant and Sheppard, 2008; Singh and Agrawal, 2010). Application of mineral- and organic fertilizers account for ~63% of the total annual Cd input to agricultural land (Luo et al., 2009). Phosphate fertilizers contain toxic heavy metals like Cd which naturally occur in phosphate rocks and minerals (Nicholson et al., 2003; Nziguheba and Smolders, 2008). Other agricultural soil Cd sources include intensive livestock production, urbanization, livestock manure, and sewage sludge (Martinez et al., 2003; Singh and Agrawal, 2008; Xiong et al., 2010). Long-term fertilizer application could cause Cd accumulation in agricultural soils (Cang et al., 2004; Nicholson et al., 2003; Xiong et al., 2010). Nevertheless, their impacts on Cd accumulation in paddy soils and rice grain are not well documented. A comprehensive assessment of Cd accumulation in paddy soil may help ensure the safe production of rice being treated with pig- or chicken manure, sewage sludge, or phosphate fertilizers. In the present study, a four-year field trial was conducted to investigate the effects of the continuous use of pig- and chicken manures, sewage sludge, and phosphate fertilizers on Cd accumulation in paddy soil and rice grain.

## 2. Field experiment validation

### 2.1. Site description

During the rice-growing seasons (early June to mid-October) between 2010 and 2013, a field trial was conducted in a rice paddy located at Changsha County, Hunan Province, China (28°08′19″N; 113°12′16″E). This region has a subtropical monsoon climate with an annual average temperature of 17.1 °C and precipitation of 1316 mm. The soil is red paddy (typical Fe-Accumuli-Stagnic Anthrosols) derived from Quaternary red clay. The soil was air-dried, passed through a 2-mm sieve and then used for basic physical and chemical properties analyses. Soil properties were determined following the methods of Bao (2000). The properties of the soil are: pH ($H_2O$), 5.19; organic matter, 31.3 $g\ kg^{-1}$; total N, 2.04 $g\ kg^{-1}$; total P, 0.85 $g\ kg^{-1}$; total K, 9.2 $g\ kg^{-1}$; available N, 212 $mg\ kg^{-1}$; available P, 11.1 $mg\ kg^{-1}$; available K, 97.0 $mg\ kg^{-1}$; and total Cd, 0.36 $mg\ kg^{-1}$.

### 2.2. Experimental design

Zhunliangyou 608 rice (*Oryza sativa* L.) was cultivated in this experiment. Four different fertilization treatments including calcium superphosphate (P), pig manure (PM), chicken manure (CM), and sewage sludge (SS), were applied at four different doses. A control (CK) with no fertilizer application was also used. The experimental design was completely randomized with three replicates per treatment. Each plot consisted of three 2.8-$m^2$ units separated from each other by rows of soil and plastic film. Prior to the onset of the experiment, a market survey was conducted to determine the Cd content of the phosphate fertilizers. From the 159 samples tested, one phosphate fertilizer (superphosphate) with a relatively high Cd level was selected, obtained from Yunan Yuntianhua International Chemical Co., Ltd, and one superphosphate with a moderate Cd content was applied to the control plants, purchased from Shangdong Xingtai hengyuan Chemical Group Co., Ltd (Huang et al., 2014). The properties of the fertilizers used in the field experiment are shown in Table 1. Total N, P, and K in calcium superphosphate, pig manure, chicken manure, and sewage sludge were determined before application. Chemical fertilizers (N as $CO(NH_2)_2$, P as superphosphate, and K as KCl) were supplied in order to establish and maintain uniform N-, P-, and K input rates for each treatment. All organic- and chemical fertilizers were spread onto the soil surface and incorporated into the soil by renovation before rice sowing. Field management (irrigation, pest control) was performed according to local conventional practices. Fertilizer application rates and element inputs are shown in Table 2. The same application rates were used every year from 2010 to 2013.

### 2.3. Plant sampling and analysis

At every annual harvest, 20 rice plants were randomly selected from each plot and were cut to ~5 cm above the ground. The plants remaining in each plot were harvested to measure their grain yield. The twenty selected rice plants were rinsed thoroughly with tap water followed by deionized water before being oven-dried at 75 °C for 48 h. The brown rice grains were then threshed out and milled.

A 0.2500-g sample of milled grain was digested with 8 mL concentrated $HNO_3$ in a microwave oven (MARS5, CEM Corp., Matthews, NC, USA). The total Cd content of the digest was determined by inductively-coupled plasma-mass spectrometry (ICP-MS) (ICP-MS 7700, Agilent Technologies, Santa Clara, CA, USA). A certified reference material (GSB-23, rice flour) and blanks were included for quality assurance. The recovery of GSB-23 was 85–105%.

### 2.4. Soil sampling and analysis

After the October 2013 rice harvest, soil samples were collected from all plots at a depth of 0–20 cm. They were air-dried at room temperature and sieved to 1 mm for the pH and available Cd determinations. Soil samples were also ground to <0.149 mm to analyze sequential Cd extraction and total soil Cd. One part soil was suspended in five parts deionized water for the pH measurement. The available Cd was assessed using diethylenetriaminepentaacetic acid (DTPA) extraction (0.005 M DTPA + 0.01 M $CaCl_2$ + 0.1 M triethanolamine (TEA), pH = 7.3). Five-gram soil samples were dispersed in 25 mL DTPA solution, shaken for 2 h, and analyzed by ICP-MS. The sequential soil Cd extraction was performed according to the methods of Tessier et al. (1979). Briefly, the Cd was segregated into five fractions: exchangeable (Exc-Cd), carbonate-bound (CB-Cd), Fe- and Mn oxide-bound (OX-Cd), organic matter-bound (OM-Cd), and residual (Res-Cd). To determine the total Cd content, the soil was digested with $HNO_3$-HF-$HClO_4$ (8:2:1 v:v:v) and the Cd levels in the extracts of each fraction and digest were determined by ICP-MS. Blanks and a certified reference material (GSBZ 50014-88) were included for quality assurance. The recovery rate was 95–110%.

### 2.5. Statistical data analysis

Analysis of variance (ANOVA) was performed with SAS v. 9.1 (SAS Institute Inc., Cary, NC, USA) (Least Significant Difference, $P < 0.05$). Data are presented as means ± SE (n = 3).