SPECIATION AND RELEASE KINETICS OF CADMIUM AND ZINC IN PADDY SOILS

by

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A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Plant and Soil Sciences

Fall 2010

ABSTRACT

Cadmium contamination in paddy soils of rice-producing countries has been reported at many locations near Zn mining and smelting plants. Cadmium in these soils can contaminate rice and subsequently enter the human food chain. Long-term Cd consumption causes chronic *Itai-itai* disease, which is characterized by renal proximal tubular dysfunction and osteomalacia. Understanding the chemical forms in which Cd and Zn are present in paddy soils is needed to develop efficient and cost-effective strategies to clean up the soils, and/or minimize Cd uptake by rice. Knowledge of metal speciation is essential because it directly controls metal mobility and bioavailability. The main goals of this study are to investigate Cd and Zn speciation and release kinetics in a paddy soil contaminated by Cd and Zn, obtained from the Mae Sot district, Tak province, Thailand. This study was conducted with a soil untreated (referred as the alkaline soil), or acidified to pH 6 and spiked with K_2SO_4 (referred as the acidified soil). These two soil samples were studied under various flooding periods and draining conditions, to mimic lowland rice culture. The secondary goal of this study is to identify the predominant low molecular weight organic acids (LMWOAs) excreted from two Thai rice cultivar under Cd stress, and to elucidate the effect of these LMWOAs on Cd and Zn desorption in the paddy soils. Synchrotron-based techniques, including bulk x-ray absorption fine structure (bulk-XAFS) spectroscopy, micro x-ray fluorescence (μ-XRF) spectroscopy, and micro x-ray absorption near-edge structure (μ-XANES) spectroscopy, and a stirred-flow

kinetic method were employed to elucidate Cd and Zn speciation, metal distribution/association, as well as Cd and Zn release kinetics, respectively.

Results from the alkaline soil revealed that, under all flooding and draining conditions, less than 25% of Cd was released during 2 hours of desorption using the strong chelating agent, DTPA-TEA-Ca. Bulk-XAFS analysis revealed that Cd carbonates were the most important species in the alkaline soil. Cadmium associated with humic acid was found in the air-dried soil and after 1 day of flooding. However, this species was not detected after 30 days of flooding. Small amounts of CdS were present after 30 days of flooding, and persisted over 150 days of flooding. Other species, e.g. Cd-kaolinite and Cd-ferrihydrite, were found after short periods of flooding, but were no longer significant after 150 days of flooding.

In the acidified soil, Cd sorbed to kaolinite was the dominant species after flooding, and its amount increased with increasing flooding periods. Cadmium sorbed to humic acid was found in the acid air-dried soil, spiked with K_2SO_4, and its amount increased after flooding. However, this species was not detected after 150 days of flooding. Flooding conditions did not cause the acidified soil to become as highly reducing as expected, which more likely due to high soluble nitrate or salinity in the acidified soil. During 2 hours of desorption using the strong chelating agent, DTPA-TEA-Ca, cumulative Cd desorption reached 100% under air-dried soil conditions, and greater than 50%, at all flooding periods and draining conditions. The μ-XRF maps showed that there was no association between Cd and Zn.

The study on Zn speciation and release kinetics showed that almost no change occurred in Zn speciation and release kinetics in the soils due to flooding or acidification, although the alkaline and acidic soils were subjected to different

flooding periods, and drained to field capacity or saturation. After 2 hours of stirred-flow experiment using the strong chelating agent, DTPA-TEA-Ca, the cumulative Zn desorption was less than 25% in all soil samples. Only two main phases were identified by LLSF, i.e. Zn-layered double hydroxides (Zn/Mg-hydrotalcite-like, and ZnAl-LDH) and Zn-phyllosilicates (Zn-kerolite). Micro-XRF maps showed that Zn was localized and associated with Cu in most samples.

The *in vitro* study on root exudates from two local Thai rice cultivars (jasmine and glutinous) under Cd stress revealed that the pH in the rhizosphere was not dependent on Cd concentration, but decreased when roots of each rice cultivar were introduced into the media. Additionally, the types and concentrations of LMWOAs secreted by the two rice cultivars were not dependent on Cd concentration. Both rice cultivars secreted three main LMWOAs, in the following order: oxalic > citric > maleic acids. The amounts of Cd and Zn released were dependent on the types and concentrations of the organic acids, and soil pH. Citric acid showed the greatest ability to desorb Cd and Zn from soil components.