Cadmium Enrichment in Paddy Rice Grain: Understanding the Effect of Soil Oxidation and Limiting the Risk through Soil and Foliar Treatments

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Abstract

Cadmium (Cd) is a non-essential element and agricultural soil contaminant (Friberg *et al.*, 1974). Cadmium accumulation in paddy rice grain is a human health risk, exacerbated by the fact that grains accumulate more Cd than the nutrients iron (Fe) and zinc (Zn), based on their relative soil concentrations (Chaney *et al.*, 1996), which enhances Cd bioavailability (McLaughlin *et al.*, 1999b). The enrichment of Cd in paddy rice grain occurs during soil oxidation, which accompanies pre-harvest drainage of the flooded paddy (Iimura, 1981b; Inahara *et al.*, 2007) and coincides with the grain-filling phase of rice growth.

The objectives of this thesis were to elucidate which soil processes are likely responsible for Cd accumulation and enrichment relative to Fe and Zn in paddy rice grain, and to determine whether soil amendments to paddy fields or foliar sprays to rice plants could be used to limit Cd accumulation and enrichment in paddy rice grain.

In Chapter 3 it is demonstrated that differential oxidation of sulfide minerals is not likely the process responsible for Cd enrichment in paddy rice grain. In Chapter 4 it is shown that when sulfide minerals form and then oxidize in a soil environment, this process in fact limits Cd solubility relative to Fe and Zn. This brings to light a new paradigm, that sulfide formation, prior to oxidation, is in fact the best-case scenario in terms of limiting Cd enrichment in paddy rice grain.

In Chapter 4 it is demonstrated that under conditions of sulfate-limitation (i.e. worst-case scenario for Cd enrichment), the Cd:Fe and Cd:Zn ratios in soil solution are lower for soil higher in Fe and/or Zn. However, in Chapter 5 it is shown that rice plants grown in soil amended with the same rates of Fe and/or Zn as in Chapter 4, produced grains with higher Cd:Fe and Cd:Zn ratios than controls. When Mn was added to soil, rice grains contained more Zn, and therefore the bioavailability of Cd was lower. When soil was amended with EDTA,

rice grains had lower Cd:Fe and Cd:Zn ratios and therefore would pose a lesser risk to human health from Cd, whereas foliar sprays of EDTA or Zn had no effect on relative accumulation of metals in grains.

This thesis addresses major knowledge gaps in the area of Cd enrichment in paddy rice. It is suggested that the relative accumulation of Cd, Fe and Zn in paddy rice grain is most likely the net effect of the oxidation of sulfide minerals and concurrent cation competition during pre-harvest drainage. It is also shown that Cd accumulation in paddy rice grain may be greater for rice grown in soils higher in Fe and Zn in the presence of chloride, and that the risk may be lesser for soils high in Mn, or amended with EDTA. Further research is suggested to support these observations under a wider range of conditions.

Declaration

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution to Jennifer de Livera and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

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- de Livera J, McLaughlin MJ, , Beak, DG, Hettiarachchi GM, Kirby JK. Release of dissolved cadmium and sulfur nanoparticles from oxidizing sulfide minerals. Soil Science Society of America Journal; article in press.
- de Livera J, McLaughlin MJ, Hettiarachchi GM, Kirby JK, Beak, DG. Cadmium solubility in paddy soils: Effects of soil oxidation, metal sulfides and competitive ions. Science of the Total Environment 2011; 409: 1489-1497

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Thesis Structure

This thesis is organized into six chapters that include two manuscripts accepted for publication in international journals (Chapters 3 and 4). The introduction and literature review (Chapter 1) outline the current understanding and knowledge gaps in determining the fate and behaviour of Cd in soils, availability to rice grains and potential impact on human health. Chapter 2 contains the thesis aims and objectives. Chapters 3 and 4 present the research findings of investigations into the solubility, lability and hence the potential availability of Cd in submerged and drained rice paddy soils. Chapter 5 presents the findings of research into limiting Cd accumulation in rice grain through the addition of competitive ions (Fe, Mn and Zn) into soils, foliar applied Zn, foliar applied EDTA and soil applied EDTA. The final chapter (Chapter 6) outlines the major findings and conclusions of the thesis and potential directions for future research.