

# Influence of Soil Properties on Zinc Solubility Dynamics Under Different Redox Conditions in Non-Calcareous Soils



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## ABSTRACT

Zinc (Zn) deficiency in paddy soils is often a problem for rice production. Flooding can decrease metal availability in some non-calcareous soils through different mechanisms associated with soil redox status. Laboratory experiments were performed in order to better understand the processes that governed the dynamics of Zn in non-calcareous paddy soils at varying redox potentials (Eh). Air-dried non-calcareous soil samples collected from four different paddy field sites in the Philippines were submerged and incubated in a reaction cell with continuous stirring and nitrogen purging for 4 weeks, and then purged with compressed air for another week to reoxidize the system. The Eh of the four soils started at 120 to 300 mV, decreased to –220 to –300 mV after 100 to 250 h of reduction, and was maintained at this low plateau for about 2 weeks before increasing again upon reoxidation. Zinc solubility showed contrasting patterns in the four soils, with two of the soils showing a decrease in soluble Zn as the Eh became low, probably due to zinc sulfide (ZnS) precipitation. In contrast, the other two soils showed that Zn solubility was maintained during the reduced phase which could be due to the competition with iron (Fe) for precipitation with sulfide. Differences in the relative amounts of S, Fe, and manganese (Mn) oxides in the four soils apparently influenced the pattern of Zn solubility after flooding.

**Key Words:** microcosm, paddy soil, precipitation, rice, soil sulfide, speciation, Zn availability

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## INTRODUCTION

Zinc (Zn) deficiency limits grain yield and nutritional content in rice and is the most common in perennially wet or calcareous soil. It is an essential nutrient for humans for the development of the immune system and gastrointestinal tract, so that an inadequate supply of Zn causes stunted physical growth, susceptibility to infections, and neurobehavioral abnormalities (Brown *et al.*, 2001). Zinc measurements on dry soil samples are ineffective in predicting Zn fertilizer responses in flooded soils (Impa and Johnson-Beebout, 2012), so it would be useful to identify other routinely measurable soil parameters that may increase our ability to predict flooding-induced Zn deficiency in rice fields.

Flooding changes many aspects of soil chemistry which are known to affect Zn availability. The primary redox-induced changes are related to the following factors: available sulfur (S) as sulfate and sulfide, amorphous iron (Fe) and manganese (Mn) (hydr)oxides, organic matter (OM), pH, and soil solution bicarbonate

concentrations (Neue and Mamaril, 1985; Du Laing *et al.*, 2009). Sulfides can decrease the mobility of trace metals such as Zn, Fe, cadmium (Cd) and copper (Cu) in soil by formation of insoluble sulfide precipitates upon flooding (Du Laing *et al.*, 2007; de Livera *et al.*, 2011). Iron and Mn (hydr)oxides provide adsorption sites that can immobilize trace metals, which can then be released under anaerobic conditions by reductive dissolution of the oxides, and adsorbed again during the reoxidation phase to less crystalline (hydr)oxides that are formed by reprecipitation (Du Laing *et al.*, 2009). Organic matter provides a source of carbon (C) for microorganisms which leads to a faster development of reducing conditions upon flooding. It also protects some metal ions (*e.g.*, Zn, Cd, nickel (Ni), and Cu) from adsorption to the solid phase through complexation with soluble humic and fulvic acids, thus increasing metal mobility (Du Laing *et al.*, 2009). Soil pH affects metal solubility by influencing the formation of metal complexes with dissolved organic C (DOC) and the adsorption of Zn, Fe, and Mn to Fe and Mn (hydr)oxides (Kirk, 2004). The formation of Zn carbonates

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may reduce Zn solubility at either high (in a calcareous soil) or low redox potential (Eh) (in any soil) due to the increase in partial pressure of CO<sub>2</sub> as OM decomposes (Kirk, 2004). Also, high bicarbonate concentrations in soil solution hinder root growth and cause root leakage of Zn-inefficient rice genotypes (Rose *et al.*, 2011).

There has been disagreement in the literature about which of these processes controls Zn solubility in flooded soils. Kittrick (1976) explained that high hydrogen sulfide (H<sub>2</sub>S) could depress Zn<sup>2+</sup> concentrations to very low levels in flooded soils by forming zinc sulfide (ZnS), while Lindsay (1979) theorized that iron pyrite (FeS<sub>2</sub>) formation should consume S when the Fe redox reactions control the equilibrium Eh at a level not favorable for ZnS formation. Subsequent studies in Zn-contaminated soils have supported both sides, confirming both that Fe can interfere with ZnS formation in sulfate-limited soils (Weber *et al.*, 2009), and ZnS can be formed in microsites (Hesterberg *et al.*, 2011). However, the relative importance of ZnS formation in Zn-limited soils is not well understood.

To isolate geochemical reactions from some of the many variables which can cause imprecise data in field experiments, reaction cells have been used to study redox chemistry questions regarding metal availability in soil (Yu *et al.*, 2007). Continuously stirred reaction cells allow precise monitoring of chemical changes in homogenized soil slurries as the Eh varies. However, stirring with continuous nitrogen (N<sub>2</sub>) purging does not allow the normal build-up of dissolved CO<sub>2</sub> in solution, and therefore does not allow meaningful measurement of carbonate equilibria (de Livera *et al.*, 2011).

Our overall aim was to understand which types of soils are likely to show flooding-induced Zn deficiency in rice. We hypothesized that although Zn does not change oxidation state due to soil Eh, Zn solubility would be influenced by other redox-active soil parameters, including changes in speciation of S, Fe, and Mn. Our objectives were to understand which chemical reactions are the most important in explaining the decrease in Zn availability in some soils after flooding and to identify a set of soil parameters that may be useful for predicting which rice fields are at risk of flooding-induced Zn deficiency.

## MATERIALS AND METHODS

### *Soil sampling*

Samples of non-calcareous soils were collected from four different paddy field sites in the Philippines: an Aeric Endoaquept from Central Mindanao University, Bukidnon (BKN) (7° N, 125° E) (Carating *et al.*,

2014); a Vertic Tropaquept from Bay, Laguna (BAY) (14° N, 121° E) (Moormann and van Breemen, 1978); an Entic Pellustert from PhilRice, Nueva Ecija (NE) (15° N, 120° E) (Cassman *et al.*, 1996); and an Aquandic Epiaquoll from the experimental farm of International Rice Research Institute, Laguna (IRRI) (14° N, 121° E) (Dobermann *et al.*, 2000). Rice of the first three sites shows moderate Zn-deficiency symptoms in most years, while the fourth site is considered as Zn-sufficient. The top 20 cm of soil was collected from each site, followed by air drying and homogenization during the grinding process to pass through a 2-mm sieve. Initial soil characterizations are shown in Table I.

### *Experimental setup*

A laboratory experiment was set up using a modified reaction cell system similar to Yu *et al.* (2007), with two replicates for each soil. The setup (Fig. 1) consisted of a 2-L reaction beaker containing 400 g soil, 1 600 mL deionized water, and 4 g ground rice straw as a source of OM (C, 391.0 g kg<sup>-1</sup>; N, 8.9 g kg<sup>-1</sup>; S, 1.05 g kg<sup>-1</sup>; Zn, 24 mg kg<sup>-1</sup>; and C/N ratio, 43.9:1). Different components were placed in the system to accommodate the measurements, including gas inlets and outlets, soil slurry sampling tubes, Rhizon Flex<sup>®</sup> soil solution samplers with pore size of 0.15 μm (Rhizosphere Research Products, the Netherlands), and in-house fabricated platinum (Pt) electrodes with a reference Ag/AgCl electrode connected to an Oakton<sup>®</sup> or Omega pHH-830<sup>®</sup> pH meter.

Slurry was stirred for 4 weeks under anaerobic conditions by continuously purging with N<sub>2</sub>, and then re-oxidized in the fifth week by purging with air. The experiment was carried out in duplicate for each soil with the addition of ZnSO<sub>4</sub>·7H<sub>2</sub>O solution to give an added concentration of 0.91 mg Zn L<sup>-1</sup> in the slurry, which is approximately equivalent to fertilization at 5 kg Zn ha<sup>-1</sup>. After 21 h of stirring, soil solution was collected in evacuated tubes using Rhizon Flex<sup>®</sup> soil solution samplers by suction. Soil solution sampling was repeated three times a week. The following parameters were measured in the soil solutions: 1) water-soluble Zn, Fe, and Mn (in samples that had been acidified immediately after sampling by adding one drop of 1 mol L<sup>-1</sup> HCl through a syringe) by atomic absorption spectroscopy (Analyst 200 Model Perkin Elmer, Singapore); 2) water-soluble sulfide (in fresh samples without acidification) by an ion-selective electrode (ISE) (USEPA, 1996b) using a 9616BNWP Model (Orion Thermo Scientific, USA) after acid-distillation (USEPA, 1996a); 3) water-soluble sulfate (in samples without acidification) by the turbidimetric method (USEPA,

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