

# Redox-related Behavior of Zinc in Noncalcareous Paddy Soils

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Adequate zinc (Zn) is found important to achieve high grain yield and nutritional quality of rice, but Zn availability sometimes decreases after flooding a rice paddy. Many aspects of soil redox chemistry can vary upon flooding, such as formation of sulfide precipitates and sorption to mineral oxides, which may control Zn solubility in soils. This study aims to understand which soil properties can best explain Zn availability at varying redox potential.

## Methods

400 g soil + 1600 mL water + 4 g ground rice straw + 0.91 mg l<sup>-1</sup> ZnSO<sub>4</sub> stirred for 4 weeks with continuous purging of nitrogen, and then reoxidized by purging air on the last week of incubation

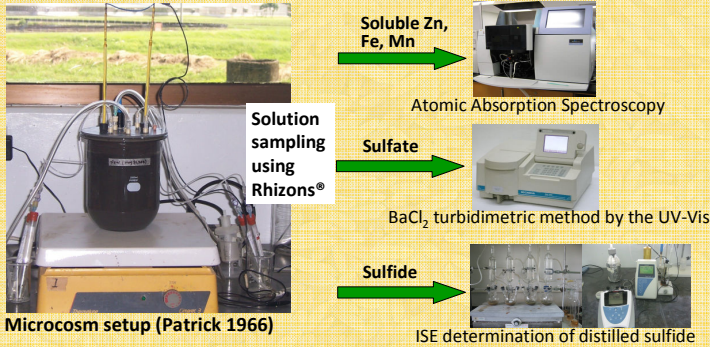


Table 1. Initial Characterization of BAY and NE soils.

Site	Organic C (%)	Texture	Amorphous Fe oxide (%)**	Amorphous Mn oxide (%)**	DTPA Zn, mg kg <sup>-1</sup>	Total S by XRF, µg g <sup>-1</sup>	pH*
BAY	4.65	silty clay loam	0.34	0.07	0.20	1110	7.0
NE	1.50	clay	1.1	0.04	1.06	231	5.2

\*1:1 soil:water ratio.

\*\* Acid ammonium oxalate in darkness (Loeppert and Inskeep 1996).

Measured data from the soil solution and initial soil characteristics were used as input parameters for geochemical equilibrium modeling using Visual Minteq (Gustafsson 2010).



## Results

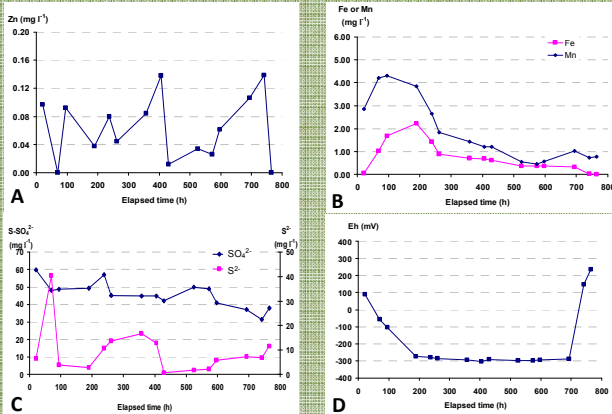


Fig. 1. The measured parameters in the BAY soil throughout the reduction period: (A) zinc, (B) iron and manganese, (C) sulfur species, and (D) redox potential.

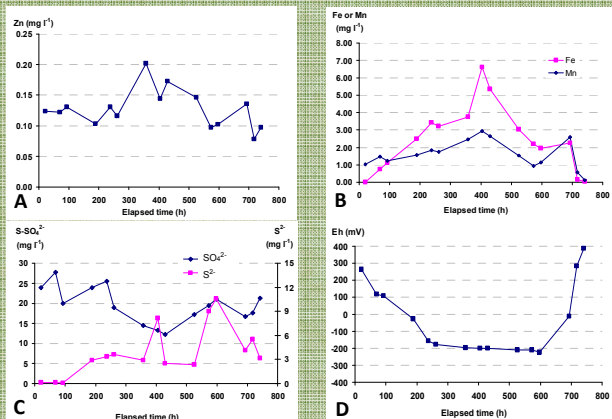


Fig. 2. The measured parameters in the NE soil throughout the reduction period: (A) zinc, (B) iron and manganese, (C) sulfur species, and (D) redox potential.

Table 2. The predominant forms of each element in the BAY soil as predicted by the equilibrium model Visual MINTEQ during each phase of reduction (de Livera 2011).

Element	Phase			
	Oxidized	Partially reduced	Fully reduced	Re-oxidized
Zn	ZnS ppt (75-99%); Zn-Mn-oxide (1-25%)	ZnS ppt (~100%)	ZnS ppt (~100%)	ZnS ppt (~100%)
S	Soluble SO <sub>4</sub> <sup>2-</sup> (60-85%); soluble S <sup>2-</sup> (1-30%); sulfate-Fe-oxide (10-20%)	Soluble SO <sub>4</sub> <sup>2-</sup> (30-60%); soluble S <sup>2-</sup> (10-40%); sulfate-Fe-oxide (20-30%)	Soluble SO <sub>4</sub> <sup>2-</sup> (40-65%); sulfate-Fe-oxide (20-30%); soluble S <sup>2-</sup> (10-30%); metal S <sup>2-</sup> ppt (6-9%)	Soluble SO <sub>4</sub> <sup>2-</sup> (50-60%); soluble S <sup>2-</sup> (25-40%); sulfate-Fe-oxide (1-10%); metal S <sup>2-</sup> ppt (6-9%)
Fe	FeS <sub>2</sub> ppt (95-99%); Soluble Fe (1-5%)	FeS <sub>2</sub> ppt (~100%)	FeS <sub>2</sub> ppt (~100%)	FeS <sub>2</sub> ppt (~100%)

- Sulfide precipitation controlled Zn and Fe availability at all time points.
- High sulfide under oxidized condition was not expected and may have been released from a sulfide-containing mineral.
- FeS<sub>2</sub> (K<sub>sp</sub> = 10<sup>-19</sup>) was favored to form with lower solubility than MnS (K<sub>sp</sub> = 10<sup>-11</sup>).
- Almost all Mn was sorbed to Mn-oxide and <1% is soluble.

Table 3. The predominant forms of each element in the NE soil as predicted by the equilibrium model Visual MINTEQ during each phase of reduction (de Livera 2011).

Element	Phase			
	Initial oxidized	Partially reduced	Fully reduced	Re-oxidized
Zn	Zn-Mn-oxide (30-80%); ZnS ppt (15-70%); soluble Zn (1-5%)	Zn-Mn-oxide (98%); soluble Zn (1-2%)	ZnS ppt (75-99%); Zn-Mn-oxide (1-25%)	Zn-Mn-oxide (90-95%); Zn-Fe-oxide (4-7%); soluble Zn (1-2%)
S	Sulfate-Fe-oxide (50-70%); soluble SO <sub>4</sub> <sup>2-</sup> (30-50%)	Sulfate-Fe-oxide (50-70%); soluble SO <sub>4</sub> <sup>2-</sup> (30-45%); metal S <sup>2-</sup> ppt (1-10%)	Soluble SO <sub>4</sub> <sup>2-</sup> (25-50%); sulfate-Fe-oxide (10-40%); metal S <sup>2-</sup> ppt (15-40%); soluble S <sup>2-</sup> (1-30%)	Sulfate-Fe-oxide (35-45%); soluble SO <sub>4</sub> <sup>2-</sup> (30-40%); metal S <sup>2-</sup> ppt (15-35%)
Fe	Soluble Fe (10-90%); FeS <sub>2</sub> ppt (10-90%)	Soluble Fe (40-95%); FeS <sub>2</sub> ppt (5-50%)	FeS <sub>2</sub> ppt (~100%)	FeS <sub>2</sub> ppt (30-85%); soluble Fe (10-60%); Fe-Fe-oxide (1-10%)

- Zn was available all throughout because of higher initial available Zn in the NE soil than in the BAY soil.
- DOC kept the Zn in solution as Zn-DOC.
- Fe dissolved upon reduction; some were bound to DOC, which kept it soluble while some formed FeS<sub>2</sub>.
- There was insufficient sulfide to bind Zn in the partially-reduced phase.

## Conclusions

Geochemical modeling of soil solution data from two contrasting soils showed that in the high-S soil, sulfide was sufficient to control both Fe<sup>2+</sup> and Zn<sup>2+</sup> solubility, even at a relatively high redox potential. In the low-S soil, there was sufficient Fe oxide to limit the formation of sulfide, except at the lowest redox potential, so most Zn remained sorbed to Mn oxide. This study gave new insights on how Zn availability could vary in different soil types as influenced by the relative amounts of S, Fe oxide and Mn oxide.

## References

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