



# Zinc solubility in tropical paddy soils: A multi-chemical extraction technique study



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## ABSTRACT

Zinc (Zn) biofortification in rice improves human nutrition and contributes considerably to rice growth. However, available information on Zn extractability and quantitative knowledge of how Zn is bound in paddy soils from Southeast Asia, which is of immense importance for Zn nutrition in rice, is rather limited. Here, we identified and quantified Zn pools with different solubility in 150 paddy soil samples using single, selective, and eight-step sequential extractions. The pH conditions of the soils ranged from ultra-acidic to slightly alkaline. The amounts of Zn in the extractable pools indicated sufficient levels of potentially available Zn (median DTPA-extractable Zn = 1.5 mg kg<sup>-1</sup>) in most soils. Chemical speciation calculations based on CaCl<sub>2</sub> extraction and DTPA-extraction data suggested that Zn<sup>2+</sup> ion activities in these soils were relatively low and most likely controlled by release of incorporated Zn rather than by dissolution of known Zn mineral phases. Maximum Zn<sup>2+</sup> solubilities were furthermore related to the solubility of franklinite (ZnFe<sub>2</sub>O<sub>4</sub>), which is controlled by the availability of Fe<sup>3+</sup> being limited by the pH-dependent solubility of Fe(III) (hydr-)oxides. Correspondingly, the sequential extraction results revealed that residual fraction (F8) and maximum acid-soluble fraction (F7) (contributed to 75% of the total Zn in soils) were the dominant Zn pools in the studied soils. The quantitative contribution of other fractions decreased in the following order: crystalline Fe oxides (F6) > Mn oxides (F3) ≈ organically bound (F4) > microcrystalline Fe oxides (F5) > mobile (F1) > mobilizable (F2). The acidic soils contained more Zn in the presumably highly mobile fraction (F1) than the neutral soils, whereas the neutral soils contained more mobilizable Zn fraction (F2) than the acidic soils. The correlation analysis suggested that the CaCl<sub>2</sub>- and DTPA-extractable Zn and Zn fractions were influenced by soil pH and soil constituents such as organic carbon, and amounts of crystalline and microcrystalline Fe/Mn oxides.

## 1. Introduction

Rice is the staple food for around 50% of the world's population, which is cultivated extensively in South and Southeast Asia. Biofortification of Zn in rice greatly affects production yield and is important for human nutrition (Phattarakul et al., 2012). Rice is, however, susceptible to Zn deficiency (Alloway, 2008), which is frequently observed in circumneutral to calcareous soils with low organic matter contents (Forno et al., 1975). Deficiency of Zn in rice was reported to be rather directly due to low available Zn content than to low total soil Zn (Rehman et al., 2012). Zinc accumulation in rice was found to be inversely related to soil pH; the more alkaline soil pH, the less Zn uptake by rice (Yoshida and Tanaka, 1969). Considering total Zn in soils, the Zn threshold for phytotoxicity in many plant species varies from 150 to 200 mg Zn kg<sup>-1</sup> and the reduction of crop yields by up to 25% in soils having total Zn contents of 100–500 mg kg<sup>-1</sup> was mainly

attributed to Zn toxicity (Kabata-Pendias, 2010). Some authors reported critical soil levels for paddy rice cultivation as extracted by DTPA ranged from 0.83 to 1.0 mg kg<sup>-1</sup> (Katyal and Agarwala, 1982; Alloway, 2008). In the Southeast Asia, a major rice production area, many soils are highly weathered, acidic soils. But little information is available on Zn availability in strongly acidic soils, which are extensively abundant in Southeast Asia and used for rice production.

The solubility of Zn in soils is mainly controlled by its chemical speciation, which can markedly vary with soil pH, redox potential ( $E_h$ ), and contents of iron, phosphorus, sulfur and natural organic matter (NOM) (Krishnamurti and Naidu, 2002; Scheinost et al., 2002; Halim et al., 2003; Jackson et al., 2003; Voegelin et al., 2003; Zeng et al., 2011). The soil pH plays a pivotal role in controlling Zn availability, solubility and speciation (Voegelin et al., 2008). High Zn solubility in acidic soils is often due to facile desorption and exchange processes on reactive surfaces of soil minerals (Scheinost et al., 2002; Voegelin et al.,

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2005) and NOM (Sauvé et al., 2000). Toxicity of Zn has been observed in strongly acidic conditions ( $\text{pH} < 3.5$ ) as present in acid sulfate soils (Reddy et al., 1995). With increasing soil pH, specific sorption of Zn to NOM, phyllosilicates, metal oxides, and carbonates becomes more relevant (Jacquat et al., 2008). Moreover, the formation of Zn precipitates as zincite ( $\text{ZnO}$ ), Zn hydroxide ( $\text{Zn(OH)}_2$ ), smithsonite ( $\text{ZnCO}_3$ ) and hydrozincite ( $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ ) in alkaline conditions can decrease Zn solubility and causes Zn deficiency, which is a major limitation for crop production in calcareous soils (Jacquat et al., 2008). Elevated concentrations of soluble Si and Al derived from the weathering of primary minerals in soils potentially decrease the solubility of Zn due to the formation of Zn-layered double hydroxide (Zn-LDH) (Voegelin et al., 2005).

Like for many other trace elements, the availability of Zn in soils has been evaluated by several single extraction procedures. These chemical extractions are straightforward, economic, and effective methods allowing us to gain invaluable data regarding the quantification of element pools available to plants (phytoavailability) and biota (bioavailability). Herein, the extractants  $\text{CaCl}_2$ , diethylenetriaminepentaacetic acid (DTPA), ethylenediamine tetraacetic acid (EDTA), and  $\text{NaNO}_3$  have frequently been used to investigate the phytoavailability of Zn and many other trace metal cations in soils. Extractions using DTPA and  $\text{CaCl}_2$  solutions were shown to provide an adequate measure for Zn availability to barley (Feng et al., 2005). Furthermore,  $\text{CaCl}_2$  extractions were applied to evaluate the availability of Zn, Pb, Ni, Cu, and Cd to *Phaseolus vulgaris*, but DTPA solution and aqua regia digestion were found to be more appropriate for assessing Cu and Pb availability (Meers et al., 2007). Mild extracting agents like  $\text{NH}_4\text{OAc}$  and  $\text{CaCl}_2$  were also shown to be useful to delineate Cd, Pb, Cu, and Zn availability to rice (i.e., both stalk and grain) in polluted soils (Zhang et al., 2010). Moreover,  $\text{CaCl}_2$  extractions were used to obtain a quantitative measure to describe Zn concentrations in the porewater in field and pot experiments (Degryse et al., 2003; Li et al., 2016).

Sequential extraction (SE) procedures are well established methods to quantify operationally-defined pools of trace elements using progressively stronger extractant solutions that attempt to stepwise dissolve metal pools from different target binding phases in soils and sediments (Tessier et al., 1979; Hedley et al., 1982; Zeien and Brümmer, 1989; Ure et al., 1993; Ma and Rao, 1997; Rauret et al., 1999; Wenzel et al., 2001; Mossop and Davidson, 2003). Various defined fractions of elements are typically acquired with the SE technique comprising fractions of water soluble and exchangeable elements, metal-organic complexes, metal sulfides, metal-carbonate precipitates, metals bound to Mn oxides, poorly ordered and crystalline Fe oxides, and metals incorporated in hardly soluble residues (Zeien and Brümmer, 1989; Rauret et al., 1999). The number of extraction steps, time, temperature, and interpretation differs with the SE schemes. The SE technique can be performed in most laboratories with a satisfactory sensitivity at trace levels. Additionally, they provide substantial information pertaining to the water soluble and the easily mobile fractions—the most available forms to biota—which are overlooked by spectroscopic techniques such as X-ray absorption spectroscopy (XAS) as they require relatively high metal concentrations in the samples (Scheinost et al., 2002; Voegelin et al., 2005). Therefore, a combination of single extractions and SEs is an essential prerequisite, and is of immense importance for identifying and quantifying different pools of Zn that are either readily available to plants or represent pools of slow long-term supply in soils.

Acid sulfate soils are extensively abundant in Thailand's central plain, 95% of which is now being used for paddy rice cultivation (Moore et al., 1990). Additionally, calcareous soils often causing Zn deficiency are found to minor extents in this area. To date, very limited information on Zn solubility is available for these agriculturally important soils. Moreover, existing data exclusively document total concentrations of trace elements (Prakongkep et al., 2008; Chittamart et al., 2010; Pongpom et al., 2014), but information on trace element availability to plants and their potential mobility in terrestrial environ-

ments is lacking. Therefore, the main purposes of our study were (i) to assess Zn solubility in tropical paddy soils from Thailand, which is one of the imperative areas for rice cultivation, using SE, and (ii) to examine the availability of Zn in these paddy soils additionally with single and selective extractions.

## 2. Materials and methods

### 2.1. Soil sampling and characterization

One hundred and fifty composite soil samples were taken from 50 paddy soils in the lower central plain of Thailand to investigate Zn solubility (Fig. 1). The studied soils were classified according to the World Reference Base of Soil Resources (IUSS Working Group WRB, 2015) as Cambisols (Ay1-Ay6, Bin, Bk1-Bk2, Bn1-Bn5, Cc1-Cc2, Ok, Rb1-Rb2, Rs1-Rs3, Sb, Se1-Se10, Tan1-Tan2, Tb, and Tr), Vertisols (Bm1-Bm2, Ck, Lb1-Lb2, Kk, Wa), Chernozems (Bl1-Bl5), and Luvisol (Ks) or respective Vertisols, Mollisols, and Alfisols according to the US Soil Taxonomy (Soil Survey Staff, 2014). Some of the locations were close to the main industrial estates (Ay3, Se4, Kk) and landfill site (Ay2) in the area. The bulk samples of surface (0–30 cm) and subsurface (30–60 and 60–100 cm) soils, about 1 kg from each horizon, were air-dried, gently pulverized, and sieved to a particle size  $< 2000 \mu\text{m}$  by a stainless steel sieve before analysis. Physicochemical properties of the soils sampled at different depths (0–30, 30–60, and 60–100 cm) were determined by standard procedures (Soil Survey Staff, 2009). The availability of Zn was assessed using single, selective, and eight-step sequential extractions.

Soil texture was determined by the pipette method after dispersion with Na-hexametaphosphate (Gee and Bauder, 1986). Soil pH was measured in water ( $\text{pH}_{\text{H}_2\text{O}}$ ) and in 1 M KCl ( $\text{pH}_{\text{KCl}}$ ) using a 1:1 (w/v) soil-to-solution ratio, and in 1 M NaF buffered at pH 8.2 using a 1:50 (w/v) soil-to-solution ratio. Organic carbon (OC) was determined by a wet oxidation procedure (Walkley and Black, 1934). Cation exchange capacity (CEC) was determined using 1 M  $\text{NH}_4\text{OAc}$  buffered at pH 7.0 (Sparks et al., 1996). Total Zn ( $\text{Zn}_t$ ) concentrations on pressed powder samples were measured by X-ray fluorescence spectrometry (S8Tiger; Bruker; Billerica, Massachusetts, USA) (Karathanasis and Hajek, 1996). The fraction of aqua regia-soluble Zn ( $\text{Zn}_{\text{aq}}$ ) was evaluated by aqua regia digestion (3:1 (v/v) of HCl and  $\text{HNO}_3$ ) (Chen and Ma, 2001) and the Zn content in digests was determined by Microwave Plasma-Atomic Emission Spectrometer (4100 MP-AES; Agilent Technologies; Santa Clara, CA, USA).

### 2.2. Quality control of total and aqua regia-soluble Zn concentrations

The accuracy of Zn concentrations was verified with a standard reference material (STSD-3; CCRMP, CANMET Mining and Mineral Sciences Laboratories; Ontario, Canada). The measured Zn concentration for total Zn and aqua regia-soluble Zn in STSD-3 was  $212 \pm 1.4$  (mean  $\pm$  standard deviation of three replicates) and  $173 \pm 6 \text{ mg kg}^{-1}$ , (mean  $\pm$  standard deviation of four replicates) which is in agreement with the certified value of  $204 \text{ mg kg}^{-1}$  and  $184 \pm 10 \text{ mg kg}^{-1}$ , respectively (Lynch, 1999).

### 2.3. Zinc availability studied with single extractions

Zinc availability in soils was examined by two single extractions using 0.01 M  $\text{CaCl}_2$  (Zn- $\text{CaCl}_2$ ) and 0.005 M DTPA (Zn-DTPA), respectively. For the  $\text{CaCl}_2$  extraction, two-grams of dried soils were mixed with 20 mL of 0.01 M  $\text{CaCl}_2$  solution and agitated on a horizontally mechanical shaker for 3 h (Novozamsky et al., 1993). The DTPA extraction solution contained 0.005 M DTPA, 0.1 M triethanolamine (TEA), and 0.01 M  $\text{CaCl}_2$  and was adjusted to pH 7.3. For the extraction, 10 g of soil sample were suspended in 20 mL of DTPA extractant solution and agitated on the mechanical shaker for 2 h (Lindsay and

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