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Full Length Article

Water Saving Irrigation Improves the Solubility and Bioavailability of Zinc in Rice Paddy

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Abstract

Fields experiment was done to investigate the effect of a typical water saving irrigation technique, namely non-flooding controlled irrigation (NFI), on the extractability, solubility, and bioavailability of zinc (Zn) in a non-polluted paddy soil. The Zn contents in the soil solutions, soil extractions by modified BCR (European Community Bureau of Reference) sequential extraction procedure, and the plant digestions were measured. Compared with the Zn in flooding irrigation (FI) soil, Zn contents in extractable (EXT) form and Zn contents in soil solutions was increased in 0–20 cm NFI soil, accompanied with a little reduction of soil Zn in oxidizable (OXD) form. That confirmed the Zn in OXD form was released into soil solution under the wetting-drying cycle condition in NFI fields, and hence resulted in high extractability and solubility of Zn in top surface soil. As a result, Zn contents in the rice plant parts in NFI fields were higher than in FI fields. It can be concluded that NFI irrigation is help to enhance soil Zn bioavailability and food Zn nutrients status in the soil without Zn-pollution and Zn deficiency, but might led to soil Zn depletion in Zn deficient soil or rice foodstuffs pollution in Zn-polluted soil.

Keywords: Zinc; water Saving irrigation; Extractability; Solubility; Bioavailability

Introduction

Zinc (Zn) is an essential micronutrient for plant and other organisms, including humans, at low concentration, and becomes a toxic heavy metal if the concentration exceeds a certain threshold (Alloway, 2008; Karami *et al*., 2014). Knowledge about the bioavailability and crop uptake of Zn in agricultural soils with different Zn levels is essential for the sustainable use of lands and crop safe production.

Generally, metals in the soil are present in several binding forms with different levels of solubility, mobility, and bioavailability. Its binding forms are effected by soil properties including pH, cation exchange capacity, oxidation–reduction status, contents of organic matter, calcium carbonate and Fe and Mn oxides (Kabra *et al*., 2007; Usman, 2008). The soil moisture condition controls both the soil redox potentials (Eh) and the biological activity, and led to change in the transformation and repartitioning of the heavy metals in soil (Shuman, 1980; Han *et al*., 2001; Tack *et al*., 2006; Makino *et al*., 2000; Zheng and Zhang, 2011; Xu *et al*., 2014) and plant uptakes (Xu *et al*., 2013a). Regarding Zn, waterlogging or flooding usually led to decrease in soil extractable Zn (Saleh *et al*., 2013). Tack *et al*. (2006) indicated that soil kept dry exhibited significantly higher soluble concentrations of Zn than field capacity and saturated treatments. Shuman (1980) indicated that air drying increases extractability of Zn at low-incubation moisture, but decreases the extractability of metals at high-incubation moisture. Zn mixed in fertilizer tended to be more labile in dry soil than in wet soil, but its diffusion was limited (Mc Beath *et al*., 2012).

Rice is one of the most important cereal crops in the Asian monsoon. Rice fields are generally kept under flooding conditions, and metals in flooded paddy soil are mostly present in the less labile fractions combined with solid-phase components (Patrick and Jugsujinda, 1992; Han and Banin, 1997; Arao *et al*., 2010). Under increasing water scarcity due to global changing, water-saving irrigation (WSI) techniques are being widely implemented in rice paddy (Mao, 2001; Bouman *et al*., 2007), which results in multiple dry-wet cycles in paddy fields and hence the change in soil biological and chemical processes (Mao, 2002). That led to changes in the transformation and repartitioning of the heavy metals in soil and its availabilities to rice plant. Dry-wet cycle or mid-season drainage in rice field frequently results in high exchangeable metals in soil solution (Liu *et al*., 2010; Xu *et al*., 2014) and high crop uptake (Zhang *et al*., 2006; Xu *et al*., 2013a). When it comes to Zn, flooded soils always have lower Zn availability than non-flooded soil (Kirk, 2004; Alloway, 2008; Rehman *et al*., 2012), short-term drainage of flooded fields or drier water management is a strategy to increase

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soil Zn availability for mitigation of Zn deficiency in most non-calcareous soil (Neue *et al*., 1998; Impa and Johnson-Beebout, 2012; Gao *et al*., 2012; Rehman *et al*., 2012; Hussain *et al.*, 2013). But in calcareous soil, Gao *et al.* (2006) found that shifting from flooded to aerobic rice cause Zn deficiency and Johnson-Beebout *et al.* (2009) reported that soil available Zn and plant Zn uptake increased with the oxidized soil treatment compared with the very anaerobic flooding soil. Gao *et al.* (2012) concluded that the contrasting results could be due to the difference in soil sulfur content and the achievable redox conditions in the two studies. The bioavailability of Zn in paddy soil was determined by many factors such as soil pH, Eh, dissolved organic matters and Fe and Mn oxides contents, the dominant processes may differ among soils and led to an apparent disagreement among studies. When paddy soil was exposed to multiple wetting-drying cycles under WSI condition, the binding forms, solubility, and bioavailability of Zn will change, but little information is available.

With a widely adopted WSI technique, non-flooding controlled irrigation (NFI), as a case, field experiment were conducted to identify the influence of NFI irrigation management on binding forms, solubility, and bioavailability of Zn in a non-polluted paddy soil.

Materials and Methods

Site Description and Experimental Design

The experiments were conducted in 2011 on the rice fields at Kunshan irrigation and drainage experimental station (31° 15′ 15″ N, 120° 57′ 43″ E) in east of China. The study area has an average annual air temperature of 15.5°C and mean annual precipitation of 1,097.1 mm. The paddy soil is Stagnic Anthrosol, developed from alluvial deposits. The properties of paddy soil and in irrigation water are listed in Table 1. The variety of rice was Japonica Rice 9314. It was transplanted with 25 cm × 13 cm hill spacing on June 28 and harvested on October 25, 2011.

Two irrigation treatments, flooding irrigation (FI) and non-flooding controlled irrigation (NFI), were established with three replications in six plots (20 m × 7 m = 140 m^2). In FI fields, 3–5 cm standing water was always maintained after transplantation except during the mid-season and harvest drainage period. In NFI fields, the flooding water (5–25 mm depth) was kept in the re-greening stage for 7–8 days; then irrigation was applied only to keep the soil saturated but not flooded, but up to 5 cm depth standing water layer was maintained during the periods of pesticide/fertilizer application or rain harvesting. The same doses of fertilizers were applied to each rice field according to the local conventional fertilizer management.

Field Measurements and Sample Analysis

Water layer depth and soil moisture were measured using a vertical fixed ruler and time–domain reflectometer (TDR, Soil Moisture, USA), to determine the time and volume of irrigation in each treatment. Fig. 1 indicated the water level and soil moisture contents in different treatment. There are 12 drying processes in NFI fields, with 65 days out of 120 days under non-flooding condition.

Soil solutions were collected by clay suction cups (2 cm in inner diameter, 7 cm in length) installed vertically at 7–14, 27–34 and 47–54 cm depths. Water samples were stored in polyethylene bottles at 4°C until analyses. At the midseason and after harvesting (August 1 and October 26), triplicate soil samples were collected at the 0–20, 20–40 and 40–60 cm soil depths from each treatment, following an S-shaped sampling pattern. The fresh soil samples were stored in a freezer before analysis. Plant samples were randomly taken from the plots on milk and yellow-ripe stages (at September 15 and October 20, respectively), and divided into five parts (root, stem, leaf, sheath and panicle). They were oven dried to a constant weight at 65°C. The dry weights were recorded, and the dried samples were ground to pass through a 1 mm sieve.

Water samples were filtered using a 0.45 μm Millipore filter and acidified with 2–3 drops nitric acid. The grounded crop samples (0.5 g) were digested at 160°C in a polyvinyl-fluoride crucible with 4 mL of concentrated HNO_3. The fresh soil samples were divided into two parts. One part (approximately 10 g in dry weight) was used to determine the soil moisture content by the oven dried method at 105°C. Another part of the fresh soil (approximately 1g in dry weight) was used for extraction of different binding forms [extractable (EXT), reducible (RED), oxidizable (OXD), and residual (RES)] Zn by using the modified BCR (European Community Bureau of Reference) sequential extraction procedure (Long *et al*., 2009), with 0.11 mol L^{-1} acetic acid, 0.1 mol L^{-1} hydroxylamine hydrochloride, 8.8 mol L^{-1} hydrogen peroxide and HNO_3-HF-$HClO_4$ as the corresponding extraction agents. The Zn contents in the soil solutions, soil extractions and the plant digestions were measured using ICP–OES (Thermo ICAP 6000 duo, Thermo Scientific). Then the Zn contents in soil and plant were calculated as the contents per unit of dry soil or plant biomass.

Results

Binding Forms of Soil Zn

Zn contents in paddy soil were almost the same at three different depths in FI and NFI fields, with the contents in 20–40 cm a little higher than in other layers (Fig. 2). The Zn in paddy soil was mostly present in RES form, followed by OXD, RED and EXT sequentially. Compared with the contents at harvest, the EXT form of Zn was higher in the midseason, which indicates that the rice plant might extract out more exchangeable Zn than its

Table 1: Properties of paddy soil and irrigation water

Item	OC	TN	TP	pH	θs			Zn		
					0-20 cm	0-30 cm	0-40 cm	0-20 cm	20-40 cm	40-60 cm
Soil	12.9 g kg^{-1}	1.03 g kg^{-1}	1.35 g kg^{-1}	6.84	0.544 cm^3 cm^{-3}	0.497 cm^3 cm^{-3}	0.478 cm^3 cm^{-3}	49.46 mg kg^{-1}	62.90 mg kg^{-1}	48.23(100*)mg kg^{-1}
Water	-	2.11 mg L^{-1}	1.02 mg L^{-1}	7.90	-	-	-	44.9-61.7 μg L^{-1} (2000**)		

OC, TN, TP, and θs are soil organic carbon, total nitrogen, total phosphorus contents, and saturated soil moisture contents
*The number is the limits of the first grade for soil pollution according to Environmental Quality Standard for Soils (GB 15618– 1995) (MEP, 1995)
** The number is the limit according to the Standards for Irrigation Water Quality (GB 5084– 2005) (GAQSIQ, 2005)

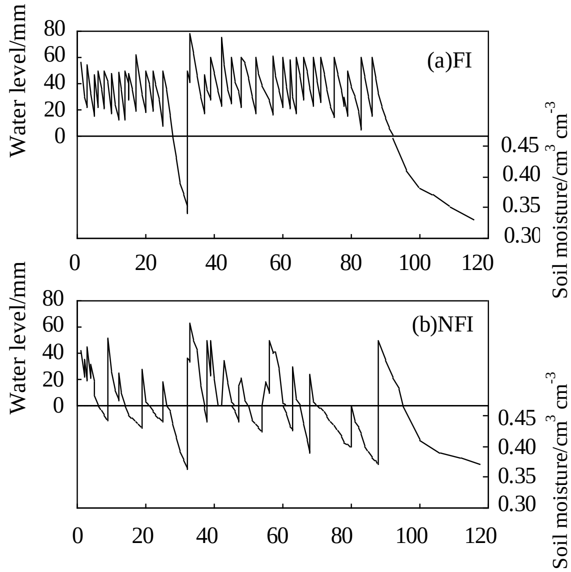


Fig. 1: Water depth and soil moisture contents in the FI and NFI rice fields

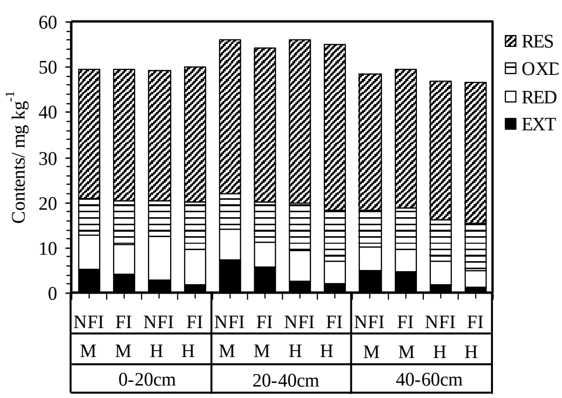


Fig. 2: Contents of Zn in different binding forms in paddy soil with different irrigation managements

transfer from other forms to EXT form. Compared with the Zn in FI soil, Zn in EXT and RED form was higher in NFI soil, and Zn in OXD form was a little lower. The difference between NFI and FI was clear in 0–20 cm and 20–40 cm soil, but not in 40–60 cm soil. The difference in EXT form of Zn between NFI and FI treatment was significant at $p<0.05$ level only in the top 0–20 cm for both measurement at midseason or harvesting, and significant at $p < 0.1$ level in the 20–40 cm for both measurement. For the RED form of Zn, the difference between the NFI and FI treatment at the depth of 20–40 cm was found significant at harvesting and midseason. For the OXD form of Zn, the difference between both treatment was found significant at $p < 0.1$ level only in the top 0–20 cm at harvesting.

Zn Contents in Soil Solutions

The Zn contents in soil solutions fell in the ranges of 14.1–111.4 μg L^{-1} (Fig. 3). Zn contents in 7–14 cm soil solutions were higher than in deep soil solutions. The contents of Zn in soil solutions were reduced over time in both NIF and FI fields. It implies that release of Zn from other binding forms into the soil solutions were less than the crop uptakes plus leaching. The Zn contents in 7–14 cm depth soil solutions were mostly higher in NFI soil solutions than in FI, except on the 21 days after transplanting. But Zn contents in 47–54 cm depth soil solutions were frequently slightly lower in NFI soil solutions than in FI. The Wilcoxon signed ranks test indicated that the differences in Zn contents soil solutions between NIF and FI treatments were significant at the confidence levels of $p = 0.12$, 0.38 and 0.04 at 7–14 cm, 27–34 cm and 47–54 cm depths. It indicated that NFI management resulted in higher release of Zn into soil solution in surface soil, but less soluble Zn move downward to deep soil. But no significant difference was found between the Zn contents in NFI and FI soil solutions at the specified depth for any specified sampling date, according to the *t*-test.

Plant Uptakes of Zn

As a result of the increased extractability and solubility of soil Zn in NFI fields, Zn contents in the rice plant parts were increased in NFI field, compared with FI fields (Fig. 4). Contents of Zn in root, stem, sheath, leaf and panicle in NFI were increased by 39.6, 15.9, 14.4, 9.2 and 5.1 mg kg^{-1} in the milky stage, and increased by 9.8, 7.6, 10.6, 2.8 and 10.2 mg kg^{-1} in the yellow-ripe stage. Among which, the differences between NFI and FI were occasionally significant at $p = 0.05$ confidence level (Fig. 4a). The uptakes by different parts of the plants also increased in NFI fields. Compared with plant Zn contents in FI plants, Zn uptakes in root, stem, sheath, leaf and panicle in NFI

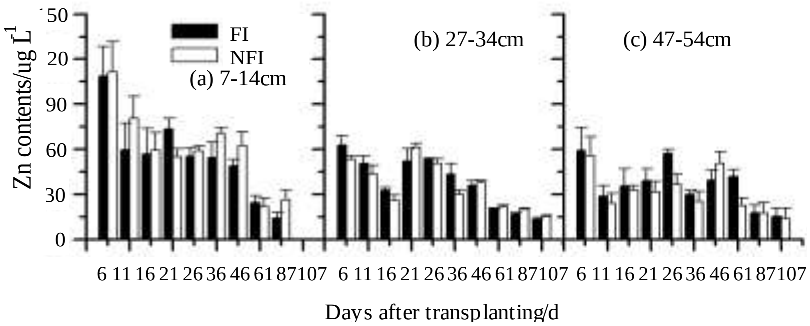
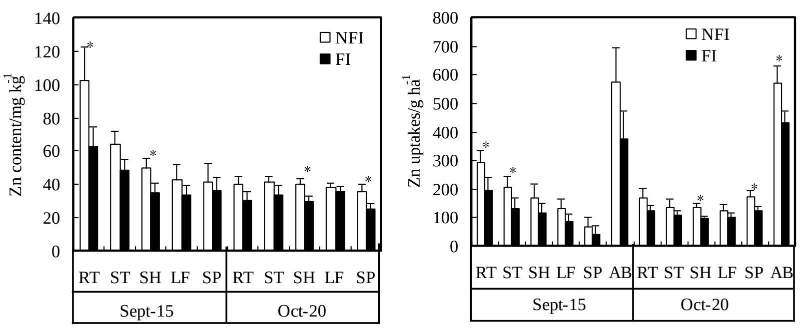


Fig. 3: Zn contents in soil solution at different depths in paddy field with different irrigation managements



(a) Zn contents in rice plant organs (b) Plant uptakes

Fig. 4: Zn contents in rice plant organs (a) and plant uptakes (b) (RT, ST, SH, LF, SP and AB means root, stem, sheath, leaf, panicle and aboveground)

plants were increased by 99.6, 75.3, 52.2, 46.9 and 26.7 g ha^{-1} in the milky stage, and increased by 45.8, 26.3, 36.8, 23.9 and 49.8 g ha^{-1} in the yellow-ripe stage. Total Zn uptakes in the aboveground parts of rice plant were estimated as 569.8 g ha^{-1} in NFI fields in the yellow-ripe stage, significantly higher than in FI field (432.9 g ha^{-1}).

Discussion

In current research, the Zn in paddy soil was mostly presents in RES form, followed by OXD, RED and EXT sequentially, it is consistent with the sequence reported by Khairiah *et al.* (2012) in a paddy soil in Malaysia. The extractability and solubility were high in top soil in NFI fields, compared with in the FI fields (Fig. 2 and 3). As a result, Zn contents in rice plant and the plant uptake was increased in NFI field (Fig. 4). Generally, under anaerobic or flooding condition, redox potential (Eh) was low, Zn in soil was more easily to be precipitated as zinc sulphide, zinc carbonate or zinc oxy-hydroxides (Kirk, 2004; Rehman *et al*., 2012; Impa and Johnson-Beebout, 2012). Under NFI condition, paddy soils were frequently suffered from the wetting-drying cycles and aerobic-anaerobic cycles (Fig. 1), that led to increase in soil Eh (Xu *et al*., 2013b) and decreased in soil reductant contents, less Zn will be precipitated or co-precipitated. At the same time, the decomposition and mineralization of soil organic matter will increase under the dry-wet conditions, and dissolved organic matter in soils will increased (Fierer and Schimel, 2002; Yao *et al*., 2011; Xu *et al*., 2013b). The dissolved organic matter in soils could increase the mobility and bioavailability of Zn in rice fields (Kashem and Singh, 2001a, b; Hernandez-Soriano and Jimenez-Lopez, 2012). The increase of EXT form of Zn in NFI paddy soils was accompanied with the decrease of Zn in OXD form, which was bounded to sulfurs or organic matter. This confirmed the Zn in OXD form released into soil solution under the wetting-drying cycle condition in NFI fields. Thus, NFI management led to high extractability, solubility and bioavailability of Zn in top surface soil, but it doesn't mean more soluble Zn leaching into groundwater because the seepage rate reduced a lot in NFI paddies (Mao, 2002; Xu *et al*., 2013b).

Since Zn in flooded paddy soils is less exchangeable and bioavailable, Zn deficiency in rice production system is more serious than other crops, and becomes a most widespread micronutrient disorder in rice production (Rehman *et al*., 2012; Gao *et al*., 2012; Impa and Johnson-Beebout, 2012). Zn is an important micronutrient for human, it was linked with function of human immune system, neuro-sensory function, reproductive health, Fe absorption and brain function (Impa and Johnson-Beebout, 2012). Rice foodstuffs were often low in Zn concentrations especially when it was produced from a Zn deficiency soil.

According to the EXT form contents in 0–20 cm soil (2.92–5.36 mg kg^{-1} in NFI soil, 1.86–4.08 mg kg in FI soil, 0.11 mol L^{-1} acetic acid extractable), the paddy soil is characterized as high Zn available, as illustrated in the map of the distribution of available Zn in soils in China by Liu (1994) and Zou *et al.* (2008). At the same time, soil Zn contents is much lower than the limits of soil heavy metal pollution according to Environmental Quality Standard for Soils (GB 15618–1995) (MEP, 1995) (Table 1). Thus, NFI irrigation helps to enhance soil Zn bioavailability and food Zn nutrients status. If the NFI was applied in a Zn deficient paddy soil, the increased solubility and bioavailability of Zn in NFI soils might be helpful for alleviating the soil and food Zn deficiency in rice production. But if the paddy soil is Zn polluted, which was frequently reported in Zn-mining region (Simmons *et al*., 2005; Zhang *et al*., 2013; Li *et al*., 2014), NFI might lead to risk of Zn metal pollution in rice foodstuffs.

The results were based on one year field experiments. Compared with Zn contents at midseason, significantly reduction in the soil EXT form Zn and Zn in solution were found at harvesting (Fig. 2 and 3), but no clear change was found in soil total Zn contents at harvesting compared with the midseason. Since more Zn was extracted out from NFI paddy soil by plant uptakes (Fig. 4), the soil total Zn contents might reduced gradually if the NFI technique was practiced in long-term. That might led to soil Zn depletion in the region without Zn deficiency, and intensify the problem in the region with Zn-deficient soil. For sustainable use of soil, additional Zn fertilizer should be applied in NFI paddy, especially in such region with soil Zn deficiency.

Conclusion

The Zn in paddy soil was mostly presents in RES form, followed by OXD, RED and EXT sequentially. Compared with the Zn in FI soil, Zn contents in EXT form and Zn contents in soil solutions was increased in 0–20 cm NFI soil, accompanied with a little reduction of soil Zn in OXD form. This confirmed that Zn in OXD form was released into soil solution under the wetting-drying cycles condition in NFI fields. Thus, NFI management led to high extractability and solubility of Zn in top surface soil, and consequently resulted in higher Zn availability to rice plant and its uptake in NFI field than in FI fields. In non-polluted paddy soil, NFI irrigation helps to enhance soil Zn bioavailability and food Zn nutrients status, but might led to soil Zn depletion.

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