

# Zinc Availability and Dynamics in the Transition from Flooded to Aerobic Rice Cultivation

**Keywords:** Soil health; Micronutrient malnutrition; *Oryza sativa*; Bioavailability; Plant nutrition; Water management; Nutrient deficiency

## Abstract

Zinc (Zn) deficiency is a fairly wide spread agronomic constraint in many of the world rice production regions. Zn deficiency inhibits several plant biological and physiological processes including carbohydrate metabolism, maintenance of cell turgidity and protein synthesis. Water scarcity is currently necessitating a shift towards non-flooded rice cultivations, which can have substantial impact on soil Zn availability. Zn availability is a function of both plant and soil factors; these could largely be influenced by the shift in water management. For example, in aerobic rice systems, iron oxidation by root-released oxygen causes reduction in rhizosphere pH. The reduced pH limits the release of Zn from highly insoluble fractions. Redox potential often increases in the aerobic cultivation, leading to iron oxidation and concomitant acidification and precipitation of  $\text{Fe}(\text{OH})_3$  onto which Zn may adsorb. The consequences of the transition in water management necessitate applying fertilizers to correct Zn deficiency and increase grain yield. This paper reviews Zn dynamics and availability in different rice growing systems. The review focuses on soil-plant processes which are influenced by the shift in water management. Fertilization strategies to correct Zn disorder and increase grain Zn content are also discussed.

## Introduction

Zn deficiency is a fairly wide spread agronomic constraint in several parts of the world rice growing regions [1]. Deficiency symptoms can be manifested as brown blotches and streaks on young leaves which can fuse to cover older leaves entirely [2]. Deficient plants grow stunted and severely deficient seedlings may not be able to recover, while those recovered are likely to show substantial delay in maturity and reduction in yield [3].

Rice water management in many parts of the world is currently undergoing significant changes shifting from flooded to non-flooded cultivations, mostly linked to water scarcity [2]. This shift can alter several soil chemical and physical properties that determine Zn availability, including pH, redox potential and soil organic matter [4]. In aerobic rice systems, for example, iron oxidation by root-released oxygen causes reduction in rhizosphere pH. The reduced pH limits the release of Zn from highly insoluble fractions [3]. Bulk soil pH may increase or decrease depending on initial soil pH, while redox potential is likely to increase causing iron oxidation and concomitant acidification with precipitation of  $\text{Fe}(\text{OH})_3$  onto which Zn may adsorb [5]. In addition, aerobic condition often accelerates organic matter oxidation, restricting Zn availability in soil solution [6]. The reduction in soil water content as a result of the change in water management is likely to restrict transpiration and diffusion. Consequently, Zn transport towards roots and its movement within the plant can be restricted [7]. The results of all these changes necessitate applying fertilizers to correct Zn deficiency and increase grain yield.



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Several different sources and method of applications are known to correct Zn deficiency in rice. The solubility and agronomic productivity of these sources, however, depends on the cultivation system practiced. For example, in flooded rice systems, Zn oxide is by large more soluble than fritted Zn [8]. The method of application can also influence the solubility; hence incorporated fertilizers can often provide higher Zn solubility over deep-placed or surface-placed fertilisers in aerobic cultivation [9]. Fertilizers which are placed on the surface are more soluble in flooded cultivations [9]. Foliar application of Zn fertilizers may provide appropriate solution to Zn solubility issues across various cropping systems since it avoids the complex soil interactions [1].

In this paper, Zn dynamics and availability in different rice growing systems are reviewed, focusing on plant-soil relations upon the shift in water management. The review also discusses the factors that influence Zn availability in paddy soils with particular emphasis on soil physical and chemical properties, and how water management shift impacts these properties. Correcting Zn deficiency via fertilization and agronomic benefits from the improved Zn nutrition is also discussed.

## Roles of Zn in Rice Plants

Zn is involved in regulating several plant biological and physiological processes. It is required for the activities of more than 300 plant enzymes [6]. These enzymes are involved in carbohydrate metabolism, maintenance of cell turgidity, protein synthesis, auxin regulation and pollen formation [6]. Therefore, stunted growth, chlorotic leaves and sterile spikes are few of the visible symptoms caused by severe Zn deficiency [6,10]. Regulation of gene expression linked to stress defense responses in plants is also Zn dependent; deficient plants are hence susceptible to injuries including excessive lights, extreme temperatures and fungal pathogen invasion [11,12].

Zn deficiency in rice is a major cause of yield losses worldwide [3]. Typical Zn concentration in rice tissues is around 35 to 100 ppm

and deficiency symptoms appears when concentration drops below 20 ppm [13]. Deficient leaves develop brown blotches and streaks; these may fuse to cover older leaves entirely [2,3]. Zn deficiency in rice reduces pollen viability leading to fewer grain set and severe yield penalties [14]. Several studies have reported deficiency symptoms in seedling in nurseries, suggesting that Zn deficiency in rice can also occur at very early stages of development [13-15].

### Zn Forms and Availability in Paddy Soils

Zn is present in soils in five distinctive forms, namely: (1) water soluble forms; (2) exchangeable forms or ions that are bound to soil particles by electrical charges; (3) organically bound forms, which are ions adsorbed, chelated or complexed with organic ligands; (4) Zn forms that are non-exchangeable sorbed onto clay minerals; and (5) forms that are linked to weathering primary minerals [11,16]. Zn in soil solution is readily available for plant roots, although its solubility can be reduced by the availability of high concentrations of phosphorous due to high applications of phosphorous fertilizers in rice growing soils [17]. Soil submergence solubilizes large amounts of Zn, making it freely accessible to roots. The solubility of Zn often decreases as soil moisture drops, forming non-exchangeable Zn complexes bound to clay particles. Recently, rice growing in many regions has shifted towards aerobic water saving systems, driven by water shortage issues. This shift in water management can alter soil conditions and affects soil Zn availability. Therefore, in order to evaluate the consequences of this shift, the subsequent sections will discuss Zn dynamics in different rice cultivation systems.

#### Flooded rice cultivation system

Water-consuming paddy rice with prolonged flooding is the most common cultivation practice in irrigated regions of the world, particularly in Asia where more than 70% of the world rice is produced [18]. Typically, rice is grown by transplanting seedlings into a plowed, harrowed paddy field which is kept flooded during most of the growing season [6,11]. Under flooded conditions, Zn deficiency often occurs two-three weeks after transplanting, resulting in large losses in productivity [2]. Several different soil properties that influence Zn availability are likely to change during flooding. For example, bulk soil pH may increase or decrease depending on initial soil pH [6]. In well-drained acid soils, submergence depletes rhizosphere oxygen, leading to reduction in redox potential and increase in soil pH [6]. In contrast, in alkaline or calcareous soils, pH is decreased after submergence, followed by concomitant chemical reduction of several metal nutrients including Zn [19]. This reduction in Zn availability is probably a result of inhibition of soil microbial activity, high phosphorus availability, precipitation of  $Zn(OH)_2$  and the decreased soil pH [20,21].

#### Aerobic rice growing system

In aerobic conditions, rice is grown as a dry field-crop in irrigated, but not flooded, fertile soils [6]. Currently, aerobic cultivation occupies approximately 20% of the total rice grown in China, Philippines and India [22]. In China, new lines of aerobic rice have recently been developed with estimated yield potential of 6-7 t ha<sup>-1</sup> [21]. Besides, water productivity (yield per unit of water used) in aerobic rice is observed to be 32-88% greater than in flooded cultivation [23]. These figures are likely to have implications

for increasing total area cultivated by aerobic rice. Switching from flooded to aerobic cultivation complicates the issue of Zn deficiency, although investigations have reported Zn deficiency in both flooded and non-flooded cultivations [3,24,25].

#### Alternate wetting and drying system

Alternate wetting and drying is water saving rice production system with maintained and sometimes enhanced grain yield compared with conventional flooded systems [26]. In this system, rice seedlings are transplanted into puddle soil and the soil kept submerged for two-three days. After that, soil surface is allowed to dry for three-four days, and the flooding resumes as ground water falls approximately 15 cm below the surface [6,11]. In this system, irrigation water is restricted by introducing periods of non-submerged conditions for several days throughout the season and this system is currently applied in East Asia including India, Vietnam and China [15].

Alternate wetting and drying is a promising system particularly in intensive rice growing regions reducing water and labor requirements [11]. However, the fluctuated moisture condition (i.e., periods of flooded/non-flooded conditions) may inhibit Zn availability in the soil and its mobility within the plant. Yang, Huang observed reduction in Zn availability in fluctuated water conditions, especially after applying organic matter [26]. Organic matter application is a common agronomic practice in rice growing regions. In alkaline and calcareous soils, those rich in organic matter, water fluctuation decreases Zn availability by adsorption to amorphous iron hydroxides and carbonate [6]. The increased level of iron, magnesium and phosphorus in soil solution and the possible immobilization of soil microbiology are potential reasons for the decreased Zn availability in water-fluctuated conditions [3,20].

#### Factors Influencing Zn Availability in Paddy Soils

The availability of Zn in soils is primarily governed by adsorption-desorption reactions and solubility relations between solution and solid phases of the soil [5]. Soil chemical and physical properties such as soil pH, redox potential, organic matter and water content exert large impact on adsorption-desorption and dissolution-precipitation reactions. Thereby, soil properties regulate the amount of Zn dissolved in soil solution [5]. The shift from flooded to non-flooded rice cultivation is likely to alter several soil properties, which may impact Zn availability. Changes in bulk soil pH and the increase in redox potential may cause iron ( $Fe^{3+}$ ) and manganese ( $Mn^{2+}$ ) oxidation with subsequent implications on Zn adsorption [15]. The increased  $Fe^{3+}$  and  $Mn^{2+}$  oxidations in aerobic conditions could precipitate Zn in forms that are not available for plants uptake [15]. Similarly, when redox potential increases,  $Fe^{3+}$  and  $Mn^{2+}$  oxidation become unstable leading to large increase in these metal concentrations [27]. Hence, the formed  $Fe^{3+}$  and  $Mn^{2+}$  become more soluble than the oxidized forms and compete with Zn for the sorption sites on the soil organic matter [11]. The released  $Fe^{3+}$  and  $Mn^{2+}$  that out compete Zn at organic matter sites is a key reason for the reduced pH in aerobic soils [15].

An inverse relationship between soil pH and Zn availability has been reported [28]. Low soil pH (acid soils; pH=5.5) increases the availability of Zn, and every unit increase in pH from 5.5 decreases

Zn availability by 35% [28]. The increased soil pH stimulates the adsorption of Zn onto soil constituents such as metal oxides and clay minerals which is linked to significant decline in Zn concentrations in soil solution and plant tissues [10,15]. Land submergence provides benefits for Zn availability as a result of adjusting bulk soil pH [29]. When alkaline soil is submerged, pH often declines since ferric iron is used as an electron receptor for oxidizing organic matter, while organic matter serves as an electron donor [2]. This reaction increases the accumulation of carbon dioxide leading to subsequent decline in soil pH [3]. The carbon dioxide produced from this reaction is retained in the flooded soil because of the restricted diffusion through the standing water on the surface. The built up carbon dioxide results in mild acidity which neutralizes soil pH and solubilises Zn [18]. The reduction-driven moderation in soil pH observed in submerged alkaline soils does not occur in aerobic soils [3,18]. This is a key difference between the two cultivation systems which may bring about significant impacts on soil health in general and Zn availability in particular [3,18,11].

Studies have shown that rice roots in flooded conditions often induce changes to rhizosphere pH in ways that acidify the soil [11,15]. This is due to the released hydrogen ion ( $H^+$ ) caused by iron oxidation which solubilizes soil Zn [11,15]. The shift towards aerobic conditions can cause an increase in soil pH due to the formation of  $Fe^{3+}$  and  $Mn^{2+}$  oxides, onto which Zn may adsorb [11]. Soils that contain less than  $0.5 \text{ mg kg}^{-1}$  exchangeable Zn are deficient [30], and the percentage of soils with exchangeable Zn larger than  $0.5 \text{ mg kg}^{-1}$  is greater in soils with pH between five and six than in soil with pH higher than seven [30]. As the shift towards aerobic rice cultivation may increase soil pH; the shift is likely to cause noticeable reduction in Zn availability [2].

Water loss through transpiration has major roles regulating Zn uptake and transport within plants [6]. Zn mobility and transport is predominantly governed by diffusion and for the plants to take up Zn water loss through transpiration most occur. The taken up Zn is then transported across the plasma membrane by ion transporter proteins. The zinc iron protein (ZIP) family are well characterized transporters facilitating Zn transport in rice roots [31]. It is believed that ZIP genes only mediate Zn transport across the plasma membrane. For the absorbed Zn to be available, it must be transported to the intracellular compartments of the cells in the plant aerial parts where it is utilised in the Zn-dependent processes [32]. Deoxy mugineic acid (DMA) and nicotianamine (NA) are well characterised Zn-transporters in rice [33]. In paddy soils, NA loses an amino group, mediated by NA amino transferase, forming 3'-keto intermediate [32]. The 3'-keto reacts with mugineic acid and loses another amino group, producing DMA. The DMA is then released into the rhizosphere by mugineic acid phytosiderophores (MAs) which binds to Zn and forms Zn-MAs complexes. These complexes are then absorbed through yellow stripe 1-like transporter protein [34]. Under flooded conditions, higher expressions of DMA related genes have been found in rice leaves than roots [35,36], hence Zn-DMA biosynthesis and transport is likely to be influenced by transpiration fluxes. The decrease in water availability as a result of the switch from flooded to non-flooded rice cultivation is likely to decrease transpiration rates. Consequently, the mass flow is restricted leading to reduction in Zn transport and loading into grains [7]. The increased shoot Zn concentration and harvest index in rice plants grown under aerobic condition after  $ZnSO_4$  applications

suggests that Zn was limiting [15], thereby; aerobic conditions can exacerbate Zn deficiency.

## Correcting Zn Deficiency via Fertilization in Paddy Soils

Zn fertilisers are commonly applied in many rice growing regions, to correct Zn deficiency and increase yield [15]. Several different Zn sources have been developed and tested in rice growing systems. The agronomic efficiency of some of these sources, however, can be influenced by the transition to aerobic rice cultivation due to the formation of insoluble Zn sulphate and frank lignite as a result of decomposition of organic matter [6]. Thereby, using suitable Zn fertiliser to match the recent water management shift is important.

Generally, Zn can directly be applied to soils as both organic and inorganic fertilizers [13]. The most commonly used form is Zn sulfide, applied as an inorganic source, due to its high solubility and low cost [30]. Zn can also be applied as Zn oxide, Zn-EDTA or Zn oxysulfate. Higher availability and transport were reported when Zn was applied as Zn-EDTA and Zn oxysulfate than Zn oxide [8]. The higher availability of Zn in Zn-EDTA and Zn oxysulfate is linked to the high solubility of these sources [37]. Results from incubation study revealed that Zn oxide dissolved rapidly causing a sharp increase, followed by a rapid decline in the soluble Zn [38]. In contrast, Zn-EDTA dissolved gradually and maintained intermediate level of soluble Zn during the nine weeks of the incubation study [25]. The gradual solubility of Zn-EDTA increases the chance of Zn being received by plant roots while decreases the chance of bounding to other insoluble complexes [25]. Due to high cost, the use of Zn-EDTA in rice farming is relatively limited [39].

There are several different methods of applying Zn fertilizers, perhaps the most common one is soil applications. Zn can be applied to soils by broadcasting, banding in seed rows or during irrigation [6]. It is often applied to soil in low land rice before flooding or soon after transplanting to prevent Zn deficiency and increase grain yield [3]. In flooded soils, plants Zn uptake is generally greater when incorporating the fertilizers with the soil than broad casting and banding [2]. In contrast, Zn use efficiency in aerobic rice is greater in surface application than deep placement [6]. Li, Zhang observed a marked increase in seedling growth, Zn uptake and grain yield when  $20 \text{ kg ha}^{-1} ZnSO_4$  was incorporated into the soil prior to flooding [40]. Zn transport in the soil is often limited and for plants to make effective use of the applied Zn it must be positionally available for seedling roots [40]. Seedling roots are only active at the soil surface. Therefore, fertilizers beneath the active root zone are often not effective [3,40].

The shift in rice water management towards aerobic systems may bring about changes to soil physical and chemical properties restricting Zn availability [3,11]. Therefore, foliar fertilizers can be more effective in non-flooded systems since it avoids the complex soil interactions [41]. In flooded cultivation, incorporating  $25 \text{ kg ZnSO}_4 \text{ ha}^{-1}$  before transplanting was more effective than spraying 0.5% (w/v)  $ZnSO_4$  [9]. Possibly because plant roots close to the surface recovered sufficient amount of Zn that became soluble after flooding to meet early growth requirements [9]. In contrast, foliar spraying of 0.5% (w/v)  $ZnSO_4$  was more effective in ameliorating Zn deficiency and increasing yield over soil application in aerobic land conditions, primarily because of the chemical changes in the aerobic soil that

make Zn unavailable for plant use [42].

Timing of fertiliser applications is another key issue determining Zn loading into grains [43]. In a field experiment, Gao found that split application of 20 kg ZnSO<sub>4</sub> ha<sup>-1</sup> (half upfront and half at tillering) resulted in higher grain yield and Zn straw content than single application [15]. Grain Zn content was only marginally increased. This suggests that, Zn application at early growth stages was agronomically effective, although showed limited effectiveness for nutritional value of the grains. Large Zn loading normally occurs when applications take place during reproductive development [30]. Joshi, Gautam observed three and four fold increase in grain Zn content when 0.5% (w/v) ZnSO<sub>4</sub> was applied at booting and anthesis stages, respectively, resulting from greater Zn translocation from flag leaves into grains [42]. Similarly, foliar application of 0.5% (w/v) ZnSO<sub>4</sub> at panicle initiation increased grain Zn content by two folds over soil application at the same stage [42]. These results suggest that Zn can be applied at several different times; although, to improve the nutritional value of the grain and achieve meaningful grain Zn, fertilisers should be applied at late reproductive stages [43].

### Agronomic Benefits from the Improved Zn Nutrition

Improving Zn content of plant seeds provide additional benefits for crop production and human health. High seed vigour and stand establishment was recorded when Zn-dense seeds were grown in Zn-deficient soils [24]. Results from field experiments with flooded rice showed that plants emerged from seeds with high Zn concentration had enhanced seedling vigour and grain yield compared with plants emerged from seeds with low Zn concentration [4,42]. In addition, it is believed that high seed Zn concentration improves plants tolerance to environmental stress during early stages of development, hence reduces the required seeding rate [24].

Adequate Zn nutrition can reduce the risk of cadmium (Cd) toxicity. In Asia, where more than 70% of the world rice is produced, high grain Cd is a growing concern [15]. Estimates of up to 50% of daily Cd consumption in Asia comes from rice [16]. Cd and Zn have comparable chemical structure, hence they compete for the same binding sites and transporter proteins [15]. Therefore, adequate Zn supply reduces Cd uptake and translocation into grains [16]. The inverse relationship between Zn and Cd is vital when investigating strategies to reducing the risk of Cd toxicity in human diets [16]. Besides, recent reports found positive linkage between dietary Zn deficiency and intestinal absorption of Cd [24,44], hence enriching crops with Zn can alleviate the risk of intestinal digestion of Cd in humans [30].

Improving Zn nutrition is also linked to lower phosphorus uptake and accumulation in grains. More than 80% of grain total phosphorus is present as phytate-major compounds capable of forming insoluble complexes binding Zn and making it less bioavailable for humans [30]. Adequate Zn nutrition decreases phytate accumulation in grains by inhibiting the expression of phosphorus-transporter genes in root cells which reduces phytate accumulation in grains [15,30,42]. Phytate-Zn molar ratio is a widely reported criterion for determining the bioavailability of Zn in diets, and keeping this ratio below 20 by supplying Zn or reducing phytate improves bioavailability of Zn in diets [42].

### Conclusions

This paper addresses an issue of growing concern regarding zinc dynamics and availability in rice following the transition towards water saving aerobic cultivation. The transition in water management is expected to cause dramatic impacts on several soil physical and chemical properties. Soil properties regulate the amount of zinc dissolved in soil solution, thereby can have large impacts on its availability in soils and transport within plants. The consequences of these changes require applying fertilisers to correct zinc deficiency and increase grain yield. However, as the transition in water management alters soil properties and reduces the solubility and agronomic productivity of various zinc sources, foliar application can avoid the complex soil interactions resulting in higher zinc availability. Therefore, careful considerations are required when correcting zinc deficiency in rice following the recent transition in water management.

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