Review Article

ZINC DYNAMICS IN SOIL, TRANSPORTATION AND ASSIMILATION IN PLANTS

ABSTRACT

The world population is expected to grow by 25% by 2050, adding another 2 billion people to the increasing burden of food demand. Food production and accessibility enriched with essential minerals may dwindle malnutrition. Currently, 2 billion people are facing micronutrient deficiency globally (Velu *et al.*, 2014). While considering micronutrient deficiencies, Zinc deficiency is a major issue for crops, humans and animals (Behera *et al.*, 2015). Notably, 50 per cent of the cultivated soils used for cereal production are reported to be Zn deficient (Das and Green, 2013).

In plants, zinc plays a key role in enzyme activation, auxin synthesis, protein synthesis, membrane integrity etc. (Tsonev and Lidon, 2012). Potential sources of zinc emission include zinc in surface water, soil and rock and anthropogenic sources of zinc like industry, human activities in agriculture, fertilization and pesticide usage (Sturikova *et al.*, 2018).

Zinc deficiency is a widespread problem in several crops because only a small fraction of the total Zn reserve becomes available during crop growth. It undergoes transformation by various mechanisms like sorption by clays, hydrous oxides, organic matter etc. which affects the availability of zinc in soils and hence the growth and nutrition of plants. Zinc is taken up into plants mainly in the form of the bivalent cation Zn^{2+} from the growing medium and assimilated by various plant parts. The transportation is mediated by membrane potential and Zn transporters are required to facilitate its diffusion across the cell membrane to the cytoplasm.

Keywords: zinc –source, status, transportation, mechanisms

Introduction

Fertility is a property inherent in the soil; it is what the soil is capable of doing if it is under the best possible conditions (Whitney, 1906). It is a key factor for successful crop production and it is a measure of capacity of soil to supply plant nutrients. It is the inherent capacity of a soil to supply essential nutrient elements to the plants in adequate amount and in right proportion of their optimum growth. Plant nutrition is the study of the chemical elements & compounds necessary for plant growth, plant metabolism & their external supply. The 17 essential plant elements include nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, boron, chlorine, iron, manganese, zinc, copper, molybdenum, and nickel.

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Zinc (Zn) is a bluish-white metallic element, accounting for about 0.02 per cent of the earth's crust. It is associated with more than 50 distinct metallo-enzymes having a diverse range

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of functions including the synthesis of nucleic acids, and specific proteins such as hormones and their receptors. Zn is involved in regulating several plant biological and physiological processes thus it is an essential micronutrient for plant growth and development. Essentiality of Zn was established by Sommer and Lipman in the year 1926 (Marschner, 1993). Unfortunately, deficiency of this metal ion has become a major agricultural problem these days. Notably 50 per cent of the cultivated soils used for cereal production are reported to be Zn deficient (Das and Green, 2013) which affects growth and development of crop plants. It also leads to severe health complications in organisms (animals and humans) that feed on produce of such deficient soils.

Sources of zinc in soil

Zinc is primarily released into the soil from minerals containing zinc oxides, sulphates, sulphides, carbonates, silicates and phosphates, which, in turn, are released from the parent rock. Other sources include atmospheric processes (bushfires, volcanic activity), biotic processes (decomposition, washing off from the surface of leaves) and, last but not least, anthropogenic activity (Noulas *et al*., 2018). Potential sources of zinc emissions are natural background levels of zinc in surface water, soil and rock; and anthropogenic sources of zinc like industry, human activities in agriculture, fertilization and pesticide using (Sturikova *et al.*, 2018).

Most of the total zinc in soils is present in association with minerals which is not easily extractable and hence not available to the plants. Therefore, the very low amount of Zn present in the soil solution is the readily available source of Zn to the plant. The general critical limit of Zn in soil and crops fall in the range of 0.6 mg kg^{-1} (DTPA-extractable) or 0.6 mg kg^{-1}(HCl-extractable) and 10-20 mg kg-1 in dry matter respectively (Katyal and Rattan, 2003).

Status of Zinc in India

Commented [R2]: Status of Zinc in India soil

In India, zinc (Zn) is now considered as fourth most important yield limiting nutrient in agricultural crops. Total Zn content in Indian soils ranges between 2 and 1,205 mg per kg (Singh, 2001). Total zinc content in Indian soils vary widely as the nature and types of soil in India are diversified. Field-scale Zn deficiency was first noticed in rice in tarai soils (Mollisols) of the foot hills of the Himalayas, which caused the complete failure of the rice crop (Nene, 1965). The average level of Zn deficiency in Indian soils is 50 per cent and is projected to increase to 63 per cent by 2025 (Singh, 2000).

Zinc dynamics in soil

A. Fractions of zinc

Zinc is found to occur in soil as:

1) Water soluble plus exchangeable zinc
2) Organically bound zinc

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3) Amorphous oxide bound zinc.
4) Crystalline oxide bound zinc.
5) Carbonate and sulphide bound zinc.
6) Manganese oxide bound zinc.

Zinc is also found as residual form in soil. On an average 60 percent of the soluble Zn in soil occurs in soluble Zn-organic complexes. Zn bearing Mineral-Smithsonite (Zn CO3), Sphalerite (ZnS), Willemite [Zn3 (PO4)2. 4 H2O], Franklinite - (Zn Fe2O4). Less than 1.75% of the total Zn occurred in bioavailable forms (Singh and Abrol, 1986).

B. Transformation of zinc in soil

Parent materials add zinc to soil solution through weathering process. Other sources of zinc supply includes mineralization of organic matter through soil microbes, desorption of clay minerals, ~~and~~ decaying and decomposition of plant materials and application of zinc fertilizer to soil. These phenomena enhance the zinc availability for plant growth. Precipitation of zinc in parent material, uptake of zinc by plants, immobilization by soil microbes, adsorption by clay mineral and leaching of zinc to ground water are responsible for release of zinc from soil solution, there by reduces the available zinc for plant growth. In this way zinc transformation occurs in soil solution. Hence these factors are taken into consideration for improving zinc status of soil (Ram, 2019).

C. Mechanisms of zinc transformation under submergence

The availability of native as well as applied Zn usually decreases and this may be partly due to the precipitation of Zn as ZnS and partly due to intense reduction of soil causing increased concentration of ferrous iron (Fe^{2+}) and manganous manganese (Mn^{2+}) in soil and ultimately enhance the condition of Zn deficiency in rice. Das (1996) reported the availability of Zn decreases due to submergence may be attributed to the following reasons:

- Formation of insoluble franklinite (Zn Fe_2O_4) in submerged soils.

$$Zn^{2+} + 2Fe^{2+} + 4\,H_2O \xrightarrow{\text{reduction}} Zn\,Fe_2O_4 \text{ (Franklinite)}$$

- Formation of very insoluble compounds of Zn as ZnS under intense reducing conditions.

$$Zn^{2+} + S^{2-} \longleftrightarrow ZnS \text{ (Sphalerite) (Insoluble)}$$

- Formation of insoluble compounds of Zn as $ZnCO_3$

$$Zn^{2+} + CO_2 \longrightarrow ZnCO3 \text{ (Smithsonite) (Insoluble)}$$

- Formation of Zn (OH)2 at a relatively higher pH

$$Zn^{2+} + 2OH^{-} \longrightarrow Zn(OH)_2 \text{ (Insoluble)}$$

- Formation of various other insoluble zinc compounds

$$\longrightarrow$$

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$Zn^{2+} + PO_4^{3-} \rightarrow Zn_3(PO_4)_2$ (Insoluble)

Singh *et al*., 1999 observed a net decrease in the total contents of the WSEX (water soluble + exchangeable), OC (organically complexed), AMOX (amorphous sesquioxide), CRYOX (crystalline sesquioxide) bound zinc in the soils upon submergence which corroborates the general observations of the occurance of zinc deficiency in wetland rice.

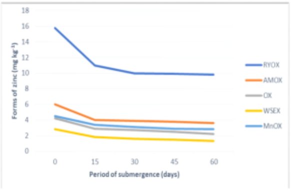

Fig. 1 Effect of submergence of different forms of native zinc (mg kg^{-1})

A. **Nutrient Interactions:** Other nutrients may interact with Zn by affecting its availability from soils and its status in the plant through the processes of growth or Zn absorption, distribution or utilization.

N × Zn

Availability of Zn increases 100 times with unit decreases in soil pH, use of acidic nitrogenous fertiliser increases Zn availability. Zinc deficiency can be increased or ameliorated in plants with the application of nitrogen fertilizers (Hafeez *et al*., 2013). Adiloglu *et al*., 2004 evaluated the effect of nitrogen fertilizer application on the availability of zinc (Zn) content in non calcic brown forest soil. The highest available Zn content of the soils was obtained from NH4Cl applied to the soils followed by (NH4)2S04.

P × Zn

High soil phosphate levels are one of the most common causes of Zn deficiency in crops encountered around the world. There are two types of interaction between P and Zn.

Type 1: Increasing P application decrease Zn concentration in shoots.

Type 2: Increasing P application do not decrease Zn concentration in shoots.

The most common type of Zn and P interaction is the type – 1 where phosphate salts bring about a decrease in Zn concentrations and usually occurs where the supply capacity of the soil for both Zn and P are marginal, so the addition of phosphatic fertiliser promotes growth sufficiently to cause the dilution of Zn concentration in plant tissues to levels which induce or enhance Zn deficiency (Prasad *et al*., 2016). However, there are other situations in which Zn deficiency has been induced by P without dilution the of Zn concentrations in plant shoots. It is likely that P must have either depressed Zn absorption by roots or the translocation of Zn from roots to the shoots.

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The zinc concentration in shoots decreased with increasing P supply in spite of the increased zinc uptake of the phosphorus induced zinc deficiency in this study is related to the dilution effect (Soltangheisi *et al.*, 2014).

Ca/Mg/K × Zn

They have antagonistic effect on Zn absorption**.** Zn absorption and translocation were reduced by 90, 60, and 20 percent because of Ca, Mg and K respectively in 21 days old rice seedlings (Sadana and Takkar, 1983). Davis-Carter *et al*. (1991) reported that Ca content in peanut leaves decreased due to Zn fertilization in some cases. The nature of inhibition of Ca, Mg and K was non-competitive.

Zn × Fe

Antagonistic, both showed a reciprocal relationship during their absorption and translocation (Hamlin and Barker, 2008)

Zn × Cu

They have antagonistic interaction (Mann and Takkar, 1983). Cu competed with Zn absorption in wheat seedlings. But it only hindered the absorption not the translocation (Brar and Sekhon, 1976).

Zn × Mn

The increase in Mn concentration in nutrient solution correspondingly increased the antagonistic effect on Zn uptake (Mann and Takkar, 1983).

Zn × Mo

Synergistic effect on Zn concentration in leaves and stems and antagonistic in the roots of cowpea.

Zn × B

The interrelationship between Boron and Zinc was synergistic in relation to changes in Zn content in soils (Prasad *et al*., 2016).

Role of zinc solubilizers

Zn uptake by plants can be increased using zinc-solubilizing bacteria. Zn solubilization by heterotrophs like strains of *Gluconacetobacter sp*., *Acinetobacter sp*., *Burkholderia sp*., *Klebsiella sp., Ralstonia sp., Bacillus sp., Pseudomonas sp., Serratia sp*., and Ericoid mycorrhizal fungi (*Oidiodendron maius*) is well-known. Many bacterial and fungal strains have been found capable of solubilizing fixed Zn and consequently increasing its uptake by plants (Imran *et al*., 2014). Effect of Zn solubilizers on the ZTI (Zinc Translocation Index) of rice varietiy super basmati was studied by (Shakeel *et al*., 2015). Highest ZTI was observed in the rice plants treated with consortium of strains (ZTI = 1.7) followed by the plants treated with only Zn (ZTI = 1.4) or consortium of strains and Zn (ZTI = 1.4). The lowest ZTI was observed in the uninoculated plants (ZTI = 1.1). This clearly shows the role of Zn

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solubilizers in Zn translocation toward rice grains.

1. Transportation of zinc to plants

Zn is taken up mainly as divalent cation (Zn^{2+} ion) by plant roots. However, in some cases, organic ligand-Zn complexes are also absorbed by plant roots (Palmgren *et al*., 2008).

A. Strategies of absorption of zinc

Depending upon the ligand secreted by plant roots, two physiological strategies are involved in uptake of Zn^{2+}. Strategy I involve efflux of reductants, organic acids and H^+ ions, which enhance solubility of Zn-complexes (Zn phosphates, hydroxides etc.) and release Zn^{2+} ions for absorption by root epidermal cells. The organic acids released either in root exudates/mucilage or directly by epidermal cells, include citric acid, malic acid, oxalic acid or tartaric acid etc. Strategy II involves efflux of Phyto siderophores (Phyto metallophores) which form stable complexes with Zn and their subsequent influx into root epidermal cells. However, this absorption mechanism (i.e. strategy II) is restricted to cereal roots. Phyto siderophores are low molecular weight organic compounds (particularly non protein amino acids such as nicotianamine, deoxymuigenic acid, avenic acid etc.) which possess high binding affinity for their respective metals resulting in their chelation and acquisition (Gupta *et al*., 2016).

B. Absorption of zinc by roots

Zn is absorbed as divalent metal ion Zn^{2+} through mass flow and diffusion mechanisms by roots. Passive Zn uptakes by these mechanisms involve participation of water (solvent) molecules and difference in Zn concentrations across root cell-plasma membrane (RCPM). The main driving force in Zn^{2+} uptake (cation uptake) is the hyperpolarization of RCPM which is mediated through activity of RCPM H^+-ATPase system. The RCPM H^+-ATPase system actively pumps H^+ ion extracellularly at the expense of ATP hydrolysis. Release of H^+ ion in rhizosphere causes hyperpolarization of RCPM on one hand while reduces the soil pH on the other hand which results in increased cation uptake rate. But unlike water, charged Zn ions are not able to cross cell membranes freely, so these divalent cations are transported by specific transporter proteins (Clemens *et al*., 2002). These proteins are not in close association with ATP breakdown which confirms passive uptake of Zn rather than active.

C. Xylem and phloem transport of zinc

After crossing the barrier of casparian strip in root endodermis; Zn^{2+} ions enter symplastically in living cells of pericycle and xylem parenchyma bordering the xylem. Another barrier in metal ion (Zn^{2+}) transport occurs at this step of nutrient transfer which is known as xylem loading. It is the key determining step in root export of metal cations. Continuous activity of H^+-ATPase in xylem parenchyma causes membrane hyperpolarization which restricts the movement of positive ions out of cytosol. Thus, loading of Zn^{2+} (metal cations) from xylem parenchyma/pericycle cells to apoplastic xylem is an active process.

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In xylem sap, metal ions such as Zn^{2+}, Ni^{2+}, Cu^{2+}, Fe^{2+} etc. are transported mainly as metal complexes with asparagines, histidine, organic acids and nicotianamine. Specialized cells are present at such transport interfaces to enhance symplastic transfer of solutes. These mainly involve transfer cells and vessel associated cells. Once Zn enters in phloem, further translocation to various plant organs and developing sinks is mediated by short and long-distance pathways. Zn is thought to be transported either in ionic form or as Zn nicotianamine, Zn-malate, Zn- histidine complexes in phloem tissues. Young sink tissues such as developing grains, tubers etc. are mainly fed by phloem (Longnecker and Robson, 1993).

D. Zinc hyperaccumulators

Zn hyperaccumulator plants can accumulate more than 10,000 ppm dry weight in their aerial parts when growing in a natural habitat (Baker and Brooks, 1989). However, only 10–20 species are reported to be Zn hyper-accumulators, with some species are also able to accumulate cadmium (Cd, which mimic to Zn) and nickel (Ni) in higher concentrations along with Zn. For example, *Arabidopsis halleri* and *Noccaea caerulescens* have the ability to accumulate extremely high concentrations of Zn of up to 13,620 and 43,710 ppm of Zn, respectively, when growing in Zn-enriched metalliferous soils (Peer *et al*., 2006). These plants can serve as models for the design of biofortification strategies. Other examples are, *Eichornia crassipes*, *Salvinia molesta*, Rapeseed, Indian mustard, Sunflower etc. Members of Brassicaceae, Amarantaceae and Asteraceae are capable of tolerating higher levels of metals in above ground parts (Reeves *et al*., 2001).

E. Nutrient penetration mechanisms at leaf surfaces and foliar Zn uptake

Foliar adsorption, cuticular penetration, diffusion in apoplastic and symplastic spaces, phloem loading into vascular veins and translocation out of the sprayed leaf tissues into other actively growing parts of the plants (Fernandez *et al*., 2013).

2. Assimilation of zinc by plants

Assimilation of nutrients by plant is the process by which nutrients acquired by plants are incorporated into the carbon constituents necessary for growth and development. The Zn content of plants varies between 30 and 100 ppm of dry matter (Marschner, 2012).

- Deficient <10-20 ppm
- Toxicity > 400 ppm

The highest concentrations are mostly found in roots, followed by rhizomes, leaves and stems. Unfortunately, concentration values are commonly used to evaluate the ‘accumulation’ of heavy metals, but this approach is not correct. In order to evaluate heavy metal accumulation, the biomass of particular plant parts must be taken into consideration. Despite substantially higher zinc concentration in the roots and the belowground biomass as compared to concentrations in the aboveground parts, the standing stock is about four times

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higher in the aboveground biomass. The major factor is the low biomass of roots and rhizomes as compared to leaves and stems (Vymazal and Brezinova, 2015).

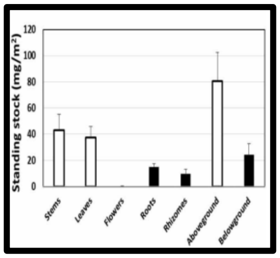

Fig. 2 Zinc standing stock (bottom) at constructed wetland Mořina, Czech Republic.

Stomph *et al*., 2014 showed that zinc taken up during grain filling was only partly transported directly to the grains and partly allocated to the leaves. Zinc taken up during grain filling and allocated to the leaves replaced zinc re-allocated from leaves to grains. The Zn level applied in the nutrient solution led to plants with a rather low plant zinc concentration towards maturity (<15 mg kg^{-1}). This low overall plant Zn concentration combined reasonable concentrations in leaves during early growth and in grains with very low stem Zn concentrations.

When plants were submitted to higher levels of Zn, increase in chlorophyll and carotenoids contents was observed (Jain *et al*., 2010). There is significant reduction in cyanogenic glucoside with Zn application compared to treatments without zinc. The economics also showed the highest net income with Zn application as well as highest benefit: cost ratio (John *et al*., 2019). Seed invigo~~u~~ration with Zn and B along with recommended dose of organic manures and nutrients increased the seed yield from 842 to 1446 kg ha^{-1} in grain cowpea (Raj *et al*., 2021).

A. Zinc deficiency in plants

Major zinc deficiency symptoms (Irshad *et al*., 2004) are stunting and resetting, interveinal chlorosis, bronzing of chlorotic leaves, dead spot over leaves including veins, tip and margins, structural aberrances in root tip and new leaves emerge white in colo~~u~~r.

Rice: Khaira disease of rice appears in 3-4-week-old seedlings which develop reddish-brown pigmentation first in middle of the leaves, then intensifies and spreads over the entire lamina. The affected leaf-area becomes papery, necrotic and entire mass of leaves collapses. Further growth of shoots, tillers and roots is arrested.

Maize: White bud of maize appear in the seedlings soon after emergence, develop light yellow colo~~u~~r in their old leaves. These leaves later develop white necrotic spots resulting into death of entire leaf. The leaves emerging thereafter remain yellow or white.

Sorghum: Deficiencies first in the younger leaves. Emerging leaves uniformly pale green. Chlorosis starting at the base progress towards the tip. Margins with distinct red line. Bleached white patches on the leaves. Older leaves have yellow streaks or chlorotic striping between veins.

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Chickpea: Chickpea plants turn small in size with few branches. The leaflets also become small in size. The leaflets of older compound leaves become light yellow in colo~~u~~r. In advance stages of deficiency, these yellow colo~~u~~r leaves get changed into reddish brown followed by bronzing and browning. Thus, there is reduction in photosynthetic efficiency and plant growth.

Tomato: In the early stages of zinc deficiency the younger leaves become yellow and pitting develops in the interveinal upper surfaces of the mature leaves. As the deficiency progress these symptoms develop into an intense interveinal necrosis but the main veins remain green, as in the symptoms of recovering iron deficiency.

Cotton: Pronounced interveinal chlorosis differs from manganese in that leaves are more misshapen, tips of leaves elongated and parallel. Both old and young leaves show red pigmentation. Leaves lose normal green colo~~u~~r of interveinal portions turn golden yellow colo~~u~~r. Brown spots extend from leaf tips to base and later dry.

Coconut: Leaflets become chlorotic, narrow and reduced in length. In acute deficiency, flowering is delayed. Zinc deficiency will also lead to button shedding.

Mottle leaf or Frenching of citrus: Newly emerging young leaves develop yellowish-green chlorotic mottling

between the veins. The leaves emerging thereafter are markedly reduced in size and turn chlorotic except near the leaf base. Under severe deficiency the shoots die-back and root growth is restricted.

B. Amelioration of zinc deficiency

Zinc deficiency can be corrected through addition of inorganic fertilizers, synthetic chelates, natural organic manures, recycling crop residues and, to some extent, by cultivation of tolerant crops and their cultivars. The effectiveness of different sources varies considerably with mode and rate of application, nutrient content, residual fertility builds up and market price. (Singh, 2008).

Zinc sulphate heptahydrate ($ZnSO_4.7H_2O$) (21–22 per cent Zn), Zn sulphate monohydrate ($ZnSO_4.H_2O$) (33 per cent Zn), sparingly soluble Zn oxide (ZnO) (67–80 per cent Zn), Zn carbonate ($ZnCO_3$) (56 per cent Zn), Zn phosphate ($Zn_3(PO_4)_2$ (50 per cent Zn), Zn frits (4–16 per cent Zn), Zn chelates (12–14 per cent Zn) and Teprosyn-Zn slurry (55 per cent Zn) are the important sources for ameliorating Zn deficiency. Zinc sulphate is the most common source of Zn in India due to its high-water solubility, easy availability and relatively low price compared with other sources and it is being widely used to correct Zn deficiency in different crops and soils (Singh, 1991). Zinc deficiency can be corrected by applying Zn through seed coating, foliar sprays or top dressing the crop, or to soil through broadcasting and band placement methods.

Table 1. Relative tolerance of crops to zinc deficiency

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SENSITIVE	MODERATELY TOLERANT	TOLERANT
Corn	Sorghum	Alfalfa
Field beans	Clover	Barley
Sweet corn	Potato	Oats
Rice	Forage	Millets
	Soybean	Rye
	Sugarbeet	Wheat
	Sudan grass	

(Singh, 2011)

C. Zinc toxicity in plants

The decrease in germination vigor and biomass are the most apparent physiological responses of plants to Zn toxicity which eventually results in decreased yield and product quality (Garg and Singh, 2018). Excess Zn affects leaves in terms of both leaf area and leaf number which might result from either inhibition in cell division or elongation or even both. Black and decayed root tips, decrease in length, surface area, diameter and volume of the root system in response to Zn toxicity have been reported in different plant species (Bernardy *et al*., 2016). The capability of biochar to ~~immobilise~~ immobilize and retain zinc (Zn) from a multi-element contaminated sediment-derived soil was explored by a column leaching experiment (Beesley and Marmiroli, 2011).

Conclusion

Zinc deficiency is a widespread problem in several crops because only a small fraction of the total Zn reserve becomes available during crop growth. Various factors affect the availability of zinc to plants, and within plant species itself the uptake of this nutrient differs. Zn is taken up into plants mainly in the form of the bivalent cation Zn^{2+} from the growing medium and assimilated by various plant parts. The transportation is mediated by membrane potential and Zn transporters are required to facilitate its diffusion across the cell membrane to the cytoplasm. Understanding the antagonistic and synergistic interaction between Zn and other nutrients is important as it also in scheduling fertilizer application. The balanced application of P and Zn is important as the antagonistic interaction is intense when compared other nutrients.

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