Review Article

Study on Zinc as Plant Nutrient- A Review

ABSTRACT

Zinc (Zn) is a very essential micronutrient which has the potential to improve nutrient use efficiency and productivity of field crops in deficient soils. In Indian soil, zinc (Zn) has been recognized as the fourth most important yield-limiting nutrient after nitrogen (N), phosphorus (P) and potassium (K). It plays a vital role in the production of biomass through its influence on diverse physiological and metabolic processes. It is responsible for formation of IAA (Auxin), acts as cofactor in many enzymes, gene expression, signal transduction, chlorophyll biosynthesis and protection against photo-oxidative damage and heat stress and resistance to infection by certain pathogen. Zinc deficiency cause yellow or white striping of the leaves maize, wheat, rice, onion, bean, sorghum *etc*., usually developing near the stalk. Plants are often stunted with shortened internodes and reddish discoloration of the nodal tissues. Due to proper managements of soil (*Like:* determination of Zn status in soil before crop sowing, source of Zn materials, definite rate of Zn application, suitable time and method of Zn application along with proper balancing of other nutrients and side by side maintain the organic matter) to improve the yield, growth and reproduction of crops under Zn deficient soils. Therefore, the present review article is to be studying on *"Study on zinc as plant nutrient"*. This finding should be encouraged to farmers and students who have involved in agricultural sectors.

1. INTRODUCTION

Indian Agriculture during the post green revolution is has witnessed the adverse effects of imbalanced and inadequate use of plant nutrients. Most of the farmers, nutrient are used largely limited to nitrogen and phosphorus, and partly to potash while other nutrients especially the secondary and micronutrients has remained neglected.

Zinc is one of the 17 essential elements necessary for the normal growth and development of plants especially at the flowering and fruit development, prolongs growth periods (Figure 1). Zinc has emerged as the most widespread micronutrient deficiency in soil and crop worldwide, resulting in severe yield losses and deterioration in nutritional quality.

In plants, zinc have main role as a structural constituent or regulatory cofactor of a widerange of different enzymes and proteins in many important biochemical pathways and these are mainly concerned with: carbohydrate metabolism, both in photosynthesis and in the conversion of sugars to starch, protein metabolism, auxin (growth regulator) metabolism, pollen formation,the maintenance of the integrity of biological membranes, the resistance to infection by certain pathogens (Alloway, 2008). By utilizing of zinc containing fertilizer, increasing the performance on quality and production of crops while shortage of this element (Zn) to decline in plant photosynthesis and cell division, and as well as the performance on quality and production of crop will be decreased (Mousavi *et al*., 2007; Efe and Yarpuz, 2011).

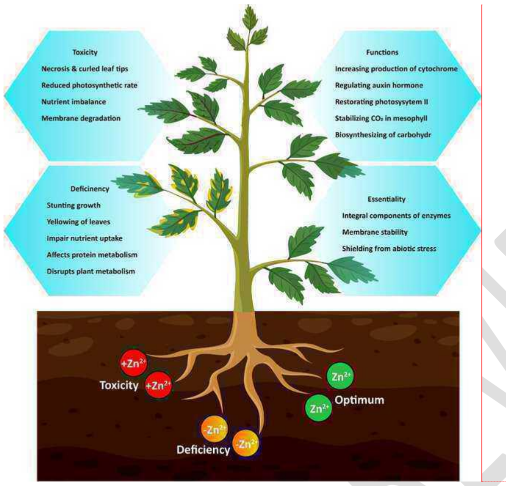

Figure 1. Role of Zinc in biochemical pathways

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Zinc (Zn) deficiency occurs in neutral and calcareous soils, intensively cropped soils, paddy soils and very poorly drained soils, sodic and saline soils, peat soils, soils with high available phosphorus (P) and silicon (Si) status, sandy soils, highly weathered, and coarse- textured soils, soils derived from serpentine and laterite, and leached, old acid sulfate soils with a small concentration of potassium (K), magnesium (Mg), and calcium (Ca) (Alloway, 2008; Akay, 2011). Crops such as bean, corn, flax, fruit trees (deciduous), grapes, hops, onions, sorghum and sweet corn are highly sensitive; barley, lettuce, potato, soybean, sudan grass, sugar beet, table beet and tomato are medium sensitive and alfalfa, asparagus, carrot, clover, grasses, oat, pea, rye and wheat are low sensitive crops to zinc deficiency (Alloway, 2008).

Application of several zinc containing fertilizers such as zinc sulfate, zinc oxide, zinc chloride, zinc sulfide and zinc carbonate can correct the zinc deficiency and improve the quality and production. Most of the farmers are unaware about the beneficial role of zinc as plant nutrient. Therefore, to ensure adequate and correct use of zinc in crop, farmers need proven and practical information directly or through farm advisory services, soil and plant testing laboratories, training programme, mass media and other sources.

2. ZINC IS ESSENTIAL FOR MUCH PLANT FUNCTION

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Zinc (Zn) is the second most abundant transition metal in living organisms after Fe. Plants taken up zinc predominantly as a divalent cation (Zn^{2+}) but at high pH it is presumable also taken up as a monovalent cation ($ZnOH^+$). Zn is an essential micronutrient for plant growth, development and reproduction that is involved in several processes:

- Acting as a cofactor for several enzyme activities
- Chlorophyll biosynthesis
- Gene expression
- Signal transduction
- Formation of Indole-Acetic-Acid (Auxin)
- Synthesis of protein and carbohydrate metabolism
- Pollen formation
- Maintenance of biological membranes
- DNA and RNA metabolisms and cell division
- Protection against photo-oxidative damage and heat stress and resistance to infection by certain pathogen.

From soil solution Zn reaches the plant root surface by three mechanisms, *i.e.*, mass flow, diffusion, and root interception. Once it is absorbed, its transportation from roots to shoots occurs through the xylem and then easily retrains-located by phloem. This transport of ions and molecules from epidermal and cortical cell to xylem occurs through the *symplastic* or *apoplastic* route. The uptake of Zn into cells and its permeability into and out of intracellular organelles require some of the specific chemicals, generally known as transporter proteins. These proteins possess a quality to span the cell membranes which facilitate the movement of zinc.

Quality of crops especially cereals and vegetables depended to a large extent on the supply of plant nutrients deficient in a particular soils. Thus, in soil with poor levels of available Zn, mainly due to high soil pH, low soil moisture and low organic matter, Soils with high leaching capacity (*e.g.*, sandy soils or those which are highly acidic) can sometimes lack Zn altogether. As a result, yellow or white striping is developed in the leaves and stalk in several crops (*i.e.*, maize, wheat, rice, onion, bean, sorghum *etc.*), plants are often stunted with shortened internodes and reddish discoloration of the nodal tissues. Therefore, require the adequate and correct application of Zn along with manures for proper quality and production of crops.

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2.1 Forms of Zinc in Soil

2.1.1 Mineral form: Zinc exists as Zinc sulphides, Zinc carbonates, and Zinc silicate. On weathering Zn ion released.

Sphalarite : ZnS
Willemite : $ZnSiO_4$
Smithsonite : $ZnCO_3$
Franklinite : $ZnFe_2O_2$

2.1.2 Adsorbed form: Zn is adsorbed on the surface of clays, oxide minerals, carbonate and organic matters.

2.1.3 Solution form: In soil solution Zn exists as Zn ion and $Zn(OH)^+$.

2.1.4 Organic complex form: Zn form stable complex with organic colloids. This form is not readily available to plants.

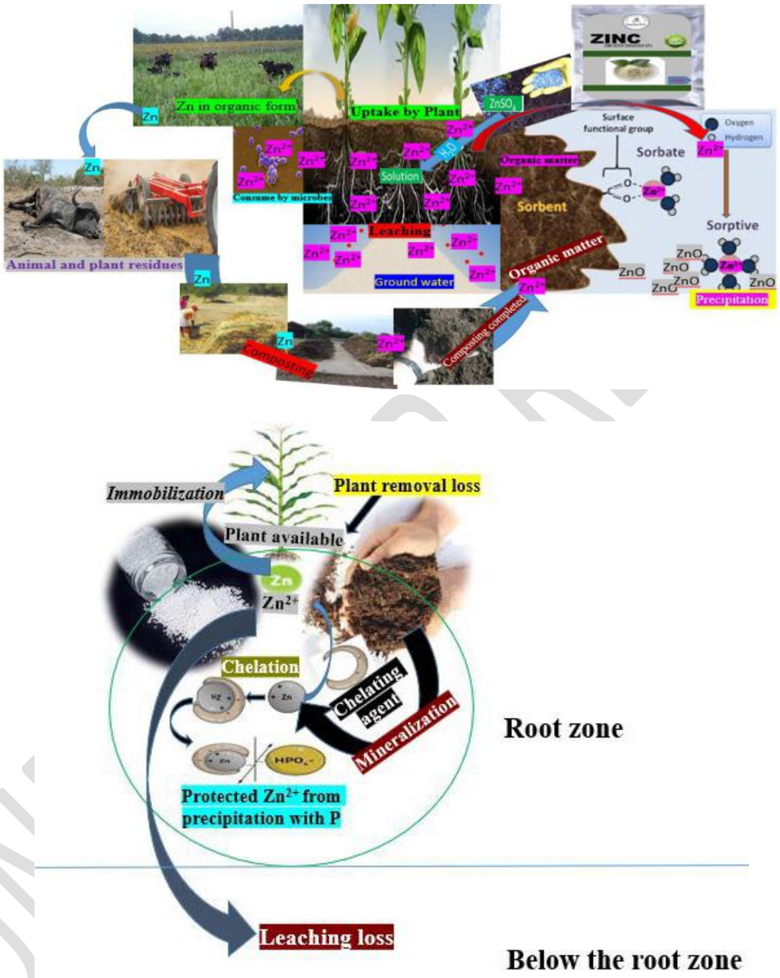


Figure 2. Scenario of distribution and mobility of Zinc in soil under climate change. (Source: Parveen *et al.*, 2024)

3. BIOCHEMICAL STUDIES ON ZINC

In biological systems, Zinc is the only metallic micronutrient that is present in the all six enzyme classes including oxidoreductases, transferases, hydrolases, lyases, isomerases and ligases (Sousa *et al.*, 2009). In these enzymes, four types of Zn-binding sites have been identified: (i) catalytic, (ii) structural, (iii) co-catalytic, and (iv) protein interface which determine the biological activity of the enzymes. In enzymes with catalytic Zn sites (e.g., carbonic anhydrase), Zn ions are coordinated to three protein ligands and one water molecule. Histidine is the most common ligand to these catalytic sites (Figure 3).

Therefore, Zn-deficient plants, the rate of protein synthesis and the protein concentration are strongly reduced, whereas amino acids accumulate, because for transcription, Zn is required in these proteins for binding to specific genes by forming tetrahedral complexes with amino acid residues of the polypeptide chain (Figure 4).

Structural Zn sites contribute to maintenance of the structure of enzymes (*e.g.*, alcohol dehydrogenase, and proteins involved in DNA replication and gene expression). In these proteins, Zn ions are mostly coordinated to four cysteine residues. Co-catalytic Zn sites are present in enzymes containing two or more Zn atoms with aspartic acid and histidine being the most common ligands in these co-catalytic sites. At the protein interface, Zn bridges proteins or subunits and affects the protein–protein interactions (Auld and Bergan, 2009; Auld, 2009). In these Zn-binding sites, the most frequent amino acid ligand is histidine, accounting for 28% of all the Zn-binding ligands. As shown in Figure 5, cysteine is the second important Zn-binding amino acid ligand and aspartic acid and glutamic acid are further important Zn ligands. Water molecules are also important Zn ligands within the protein structure.

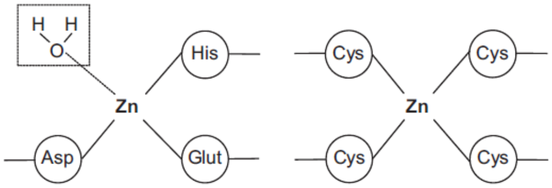


Figure 3 Protein ligands

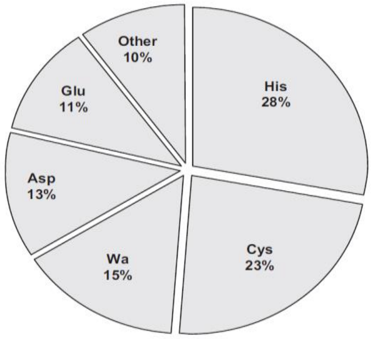


Figure 5. Overview of the percentage of Zn-binding ligands in the Zn proteome as present in the Protein Data Bank. Asp: aspartic acid; His: histidine; Cys: cysteine; Glu: glutamic acid; Wa: water

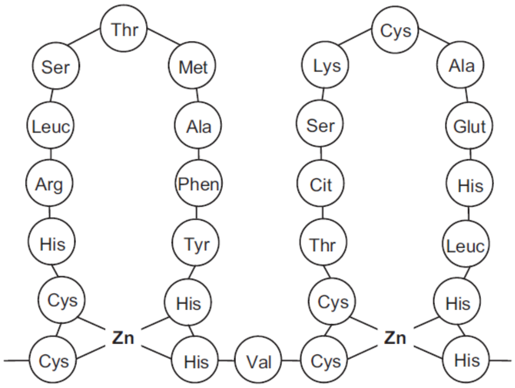


Figure 4. Schematic presentation of role of Zn in tertiary structure of the peptide chain in replication proteins (‘zinc finger’). Based on Coleman, 1992 and Vallee and Falchuk, 1993.

[Sousa *et al*. (2009) with permission from the Royal Society of Chemistry].

Zn is an essential structural component of several enzymes like Cu/Zn superoxide dismutase (SOD), Alcohol dehydrogenase and carbonic anhydrase (CA) (Singh *et al*., 2005). The activities of these enzymes may be used as indicators of Zn deficiency in plants. Generally, lower levels of Zn decreased the activities of these enzymes in many species (Kabir *et al.*, 2014). A Zn-efficient wheat genotype showed decreased activity of CA compared to a Zn-inefficient genotype in Zn deficiency condition (Rengel, 1995). The expression and activities of the Zn requiring enzymes Cu/Zn SOD and CA were also associated with Zn-efficient genotypes of wheat (Hacisalihoglu *et al.,* 2003). Expression levels of Cu/Zn SOD were elevated in Zn-efficient genotypes of wheat (Hacisalihoglu *et al.,* 2003). The activities of these enzymes were also decreased in *Vinga mungo* (black gram) during Zn deficiency (Pandey *et al.*, 2002). Similar responses were obtained in enzyme studies in bread wheat, durum wheat and rye in Zn deficiency (Cakmak *et al.*, 1997a). Further molecular studies confirmed that expression of Cu/Zn SOD genes was induced in Zn-efficient wheat genotypes compared to Zn-inefficient genotypes in Zn deficiency (Hacisalihoglu and Kochian, 2003).

Plant root exudates can help overcome Zn deficiency by increasing the bioavailability of Zn to plants. The genotypic difference in Zn acquisition from the soil may be linked to composition of root exudates released by each genotype (Marschener, 1998). The low molecular weight organic acids such as citrate, malate, nitric oxide, oxalic acid, acetic acid and amber acid are involved in the mobilization of Zn under Zn deficiency (Li *et al.*, 2012). Similarly, citrate efflux also helps uptake higher amount of Zn in low Zn, and the process is genotype dependent in rice (Hoffland *et al.*, 2006). Studies in rice confirmed that release of low molecular weight organic acid anion like malate was increased by up to 64% in low Zn supply compared to adequate Zn supply (Gao *et al.*, 2009). These studies provided evidence that root exudates helped improve Zn uptake during Zn deficiency. Identification of genotypes with efficient release of organic acid anion may help uptake Zn more efficiently in low Zn conditions. Similarly, phytosiderophores helped uptake Zn more efficiently in low Zn conditions in barley (Erenoglu *et al.*, 2000). Crop plants like sorghum and wheat significantly increased phytosiderophore efflux in response to Zn deficiency (Hopkins *et al.*, 1998).

4. MECHANISM OF ZINC UPTAKE AND TRANSLOCATION IN PLANTS

Zinc is absorbed from soil as Zn^{2+} and transported through xylem to shoot (Clemens, 2001; Hart *et al.,* 1998). Zn is transported from soil through the root plasma membrane. The rate of Zn uptake depends on uptake efficiency of the root system, Zn concentration at the root surface and permeability of the cell membrane (Shukla *et al.*, 2014). Zinc enters the plant from the soil through membrane bound transporters (Hacisalihoglu and Kochian, 2003). These transporters are involved in absorption of Zn from the soil, transport within the plant, xylem loading and unloading, vacuolar sequestration and remobilization from the vacuole. Many types of Zn transporters have been identified and their function has been characterized in plants (Figure 6; Table 1).

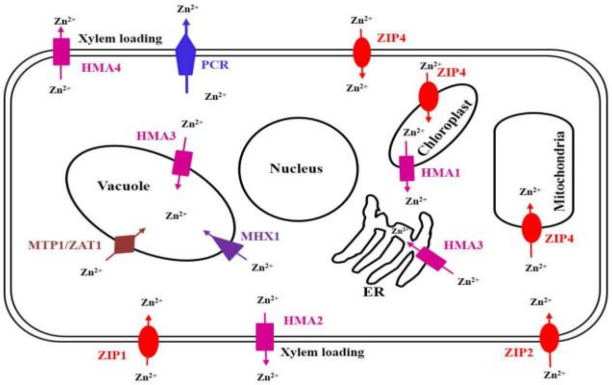
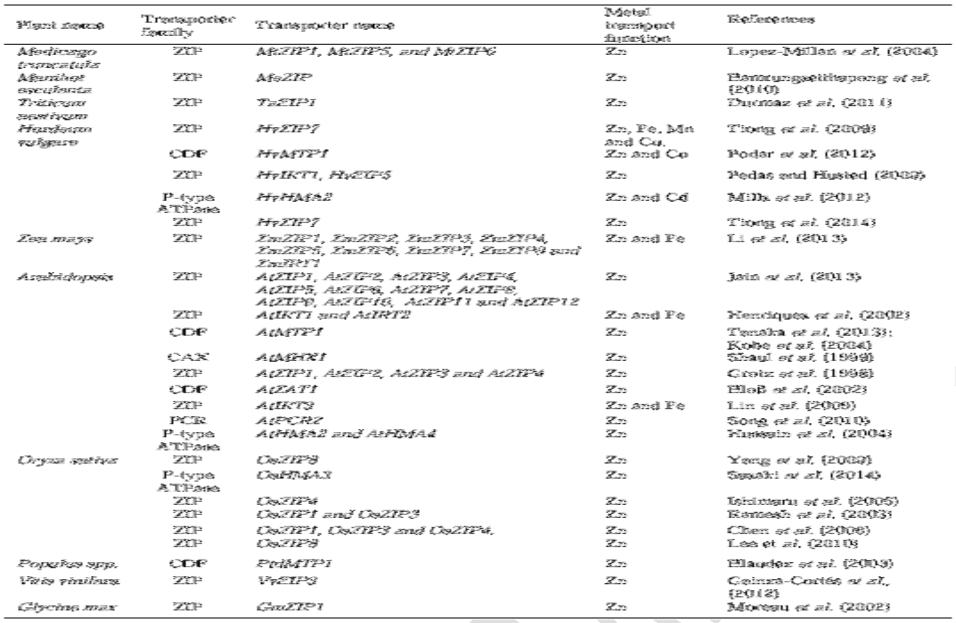


Figure 6. Localization of various Zn transporters in plant cell. Zn transporter family is actively involved in uptake, transport, detoxification and homeostasis of Zn within plants. Depending on the Zn concentration in soil, various types of Zn transporters are expressed. During deficient concentration of Zn, ZIP (ZIP1, ZIP2 and ZIP4) and P-Type ATPase (HMA2) families of Zn transporters are induced which transport Zn into the cell through plasma membrane from the soil, and then CAX (MHX1), CDF (MTP1 and ZAT1), P-Type ATPase (HMA2 and HMA4) and ZIP (ZIP4) families of transporters are involved in mobilization of Zn into organelles. The PCR family member PCR2 is important for redistribution and detoxification Zn. The P-Type ATPase family member HMA1 is involved in detoxification of Zn in chloroplast. Studies on localization and transport activity of ZIP transporters are still under progress (***Source:*** Ajeesh Krishna *et al.*, 2017).

Table 1: Details of various Zn transporters reported in plants.



Plant name	Transporter family	Transporter name	Metal transport function	References
Medicago truncatula	ZIP	*MtZIP1, MtZIP5, and MtZIP6*	Zn	Lopez-Millan *et al.* (2004)
Manihot esculenta	ZIP	*MeZIP*	Zn	Bamrungsetthapong *et al.* (2010)
Triticum aestivum	ZIP	*TaZIP1*	Zn	Durmaz *et al.* (2011)
Hordeum vulgare	ZIP	*HvZIP7*	Zn, Fe, Mn and Cu.	Tiong *et al.* (2009)
	CDF	*HvMTP1*	Zn and Co	Podar *et al.* (2012)
	ZIP	*HvIRT1, HvZIP5*	Zn	Pedas and Husted (2009)
	P-type ATPase	*HvHMA2*	Zn and Cd	Mills *et al.* (2012)
	ZIP	*HvZIP7*	Zn	Tiong *et al.* (2014)
Zea mays	ZIP	*ZmZIP1, ZmZIP2, ZmZIP3, ZmZIP4, ZmZIP5, ZmZIP6, ZmZIP7, ZmZIP8 and ZmIRT1*	Zn and Fe	Li *et al.* (2013)
Arabidopsis	ZIP	*AtZIP1, AtZIP2, AtZIP3, AtZIP4, AtZIP5, AtZIP6, AtZIP7, AtZIP8, AtZIP9, AtZIP10, AtZIP11 and AtZIP12*	Zn	Jain *et al.* (2013)
	ZIP	*AtIRT1 and AtIRT2*	Zn and Fe	Henriques *et al.* (2002)
	CDF	*AtMTP1*	Zn	Tanaka *et al.* (2013); Kobe *et al.* (2004)
	CAX	*AtMHX1*	Zn	Shaul *et al.* (1999)
	ZIP	*AtZIP1, AtZIP2, AtZIP3 and AtZIP4*	Zn	Grotz *et al.* (1998)
	CDF	*AtZAT1*	Zn	Bloß *et al.* (2002)
	ZIP	*AtIRT3*	Zn and Fe	Lin *et al.* (2009)
	PCR	*AtPCR2*	Zn	Song *et al.* (2010)
	P-type ATPase	*AtHMA2 and AtHMA4*	Zn	Hussain *et al.* (2004)
Oryza sativa	ZIP	*OsZIP8*	Zn	Yang *et al.* (2009)
	P-type ATPase	*OsHMA3*	Zn	Sasaki *et al.* (2014)
	ZIP	*OsZIP4*	Zn	Ishimaru *et al.* (2005)
	ZIP	*OsZIP1 and OsZIP3*	Zn	Ramesh *et al.* (2003)
	ZIP	*OsZIP1, OsZIP3 and OsZIP4.*	Zn	Chen *et al.* (2008)
	ZIP	*OsZIP8*	Zn	Lee et *al.* (2010)
Populus spp.	CDF	*PtdMTP1*	Zn	Blaudez *et al.* (2003)
Vitis vinifera	ZIP	*VvZIP3*	Zn	Gainza-Cortés *et al.*, (2012)
Glycine max	ZIP	*GmZIP1*	Zn	Moreau *et al.* (2002)

Source: Ajeesh Krishna *et al.*, 2017

5. SOIL FACTORS, WHERE ZINC DEFICIENCY MAY OCCUR

Although genotypic factors are important in determining either tolerance or susceptibility of a crop cultivar to zinc deficiency, it is soil factors which are responsible for low available zinc supply. In general, the soils most commonly associated with zinc deficiency problems in plants mainly due to the factors like neutral to alkaline in reaction, especially where the pH is above 7.4, high calcium carbonate content in topsoil or in subsoil exposed by removal of the topsoil during field leveling or by erosion, coarse texture (sandy soil) with a low organic matter status, permanently or intermittently waterlogged soil, high available phosphate status, high bicarbonate or magnesium concentrations in soil or irrigation water and acid soil of low zinc status developed on highly weathered parent material (Figure 7).

Major Zn deficiency causes include: (i) Soils of low Zn content (Parent material), (ii) soils with Restricted Zones, (iii) pH, (iv) soils low in organic matter, (v) Microbially inactivated Zn, (vi) Cool soil temperature, (vii) Plant species and genotypes (viii) High level of available phosphorus and (ix) Effects of nitrogen. Zn deficiency problems may occurs in soils with the subsequent characters; (a) strongly alkaline in reaction (b) high phosphorus status by application of phosphatic fertilizers may reduce use of zinc (c) leached sandy soils (d) acid soils of low total Zn status developed on highly weathered parent material (e) calcareous soil (f) peat and muck soils (g) permanently wet (water logged) and (h) high bicarbonate and magnesium in soils or irrigated water.

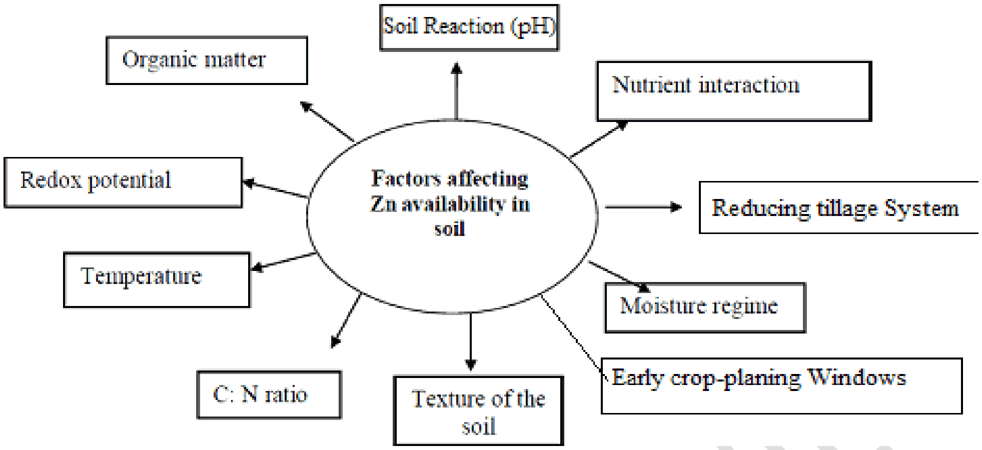


Figure 7: Important soil chemical and physical factors for affecting the amount of zinc and its availability in soil

5.1 Parent Material of Soils and Zn Content

The concentration of Zn in soils is mostly dependent on soil parent materials. When the soils are originated from gneisses, granites, sandstone and limestone can be lower in Zn contents. Soils originating from igneous rocks are higher in zinc (Pendias and Pendias, 1992 & Barak and Helmke, 1993). In contrast, soil containing high Quartz (Sand) and highly leached acid soil to dilute the soil Zn concentrations resulting very low in plant Zn availability (Brehler et al., 1978). Zinc deficiency also may occur in such soils which are inherently low in Zn. The problem is that only a small amount of soil Zn is available to the crop because of one or more adverse factors. The remainder of the total Zn is fixed in the soil in an insoluble or un-exchangeable form and difficult to make available to crop (Stahl and James, 1991).

5.2 Soil Reaction (pH)

Zinc availability is highly dependent on soil reaction. Zinc is easily available in acidic condition but in very high acidic condition their availability increases to such as extent that they become Toxic to plants. Their availability decreases with an increases in pH and very low after pH 7.0. The concentration of Zn in the soil solution decreases from 10^{-4} (6.5 µg g^{-1}) to 10^{-10} M (0.007 µg L^{-1}) with an increase from pH 5 to pH 8 (Kiekens, 1995). The Presence of higher carbonate contents in alkaline soils also absorb Zn and hold it in an un-exchangeable form (Udo et al., 1970). The main types of salt affected soils are the saline soils (*Solonchaks*), sodic soils (*Solonetz*) and both mainly occur in arid and semi-arid regions. Saline soils contain high concentrations of soluble salts which restrict the types of crops which can be grown and reduces the availability of zinc. In the case of soils characterized by high contents of hydroxyl ($^{-}$OH) ions, it is difficult to get a crop response even to applied Zn. Zn under alkaline conditions is attributed to the precipitation of Zn as $Zn(OH)_2$ or $ZnCO_3$ (Shukla and Mittal, 1979 & Saeed and Fox, 1977). Liming of acidic soils increases pH and also the Zn fixing capacity, particularly in soils with high P levels (Alloway, 2004). However, soils with low pH and calcite are common in tropical regions and should be limed to increase cereal production (Fageria and Stone 2008). In summary, high soil pH/alkaline soils are linked to Zn sorption on carbonates, hydroxides and clay minerals, and thus limit Zn uptake by plants. The best pH for their availability is 4.5 to 6.5.

5.3 Soil temperature

Soil temperature also influences Zn availability as wet and cool seasons result in reduced Zn availability due to the reduced rate of soil mineralization (i.e. the liberation of Zn in organic matter by decomposition (Takkar and Walker, 1993). Zinc deficiency is exacerbated in cool seasons as low temperatures restrict organic matter decomposition, root growth (Alloway, 2008) and mycorrhizal colonization, which further limit plant Zn uptake. Temperatures below 16ºC during growth caused decreased Zn uptake in maize tops (Ellis, 1995). While in warm and moist soils, Zn uptake was higher in rice than in maize (*Zea mays* L.) (Bauer and Lindsay, 1965). Moreover, adverse climatic conditions such as drought or compaction which can cause Zn deficiency in plants (Alloway, 2008).

5.4 Reduced-tillage systems

Crop residues on the soil surface at planting time shade the soil, resulting in a lower soil temperature and higher soil moisture level. These conditions put stress on a small root system, making it difficult to uptake required Zn, as well as P and Mg.

5.5 Soil organic matter

Zinc deficiency is prevalent in soils, which are naturally high or low in organic carbon, waterlogged, or light-textured (Ahmad *et al*., 2012). Soil organic matter is an important soil constituent which originates from decomposition of animal and plant products. The most stable organic compounds in soil are humic substances (i.e., humic and fulvic acids) contain a relatively large number of functional groups (OH, COOH, SH) which have a great affinity for metal ions such as Zn^{2+}. Fulvic acids mainly form chelates with Zn over a wide pH range and increases the solubility and mobility of Zn (Gurpreet-Kaur *et al*., 2013). Simple organic compounds such as amino acids, hydroxy acids and also phosphoric acids are effective in complexing Zn, thus increasing its mobility and solubility in soils (Alloway, 2008). Therefore, increase in the organic matter contents in soil will increase the Zn availability. However, if the organic matter content in soil is too high, like in peat and muck soils, this can also contribute to Zn deficiency due to the binding of Zn on solid state humic substances. Alloway (2008) noted a significant positive correlation between soil extractable Zn and soil organic matter content. Mandal *et al.* (1988) reported that the addition of organic matter increased Zn bioavailability to rice plants.

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5.6 Early crop-planting windows

Sowing of seed corn and certain vegetables earlier in the spring, when soils are cool and moist. This compounds the stress on seedlings caused by reduced tillage and makes a readily available supply of Zn and other nutrients even more important to ensure early plant growth.

5.7 Moisture regime

Plants become more sensitive to Zn deficiency under low water availability. Under limited water supply, Zn movement in the soil is limited that restricts the Zn uptake by plants (Marschner, 2012). The poor availability of zinc caused by water logging can be due to a relatively high pH, zinc being present as the insoluble sulphide (ZnS) and elevated concentrations of ferrous, bicarbonate, and phosphate ions (Doberman and Fairhurst, 2000). For example, rice plants under submerged conditions suffer from Zn deficiency in calcareous soils. But wheat grown in the same soil following rice grows normally (Kausar *et al*., 1976). Zinc deficiency due to flooding was a result of Zn reaction with free sulphide (Mikkelsem and Shiou, 1977). Under the submerged conditions of rice cultivation, Zn is changed into amorphous sesquioxide precipitates or franklinite; $ZnFe_2O_4$ (Sajwan and Lindsay, 1988 & Singh and Abrol, 1986). Thus a delay in Zn application until after flooding for rice minimizes Zn fixation by sesquioxides (Mandal and Mandal, 1986). Moreover, several studies concluded that the growth of Zn deficient plants is poor under water-limited conditions and that the sensitivity to Zn deficiency is more pronounced when plants are drought-stressed (Hajiboland and Amirazad, 2010). These studies also pointed out that, in drought-stressed plants, the effect of irrigation on grain yield is maximized with adequate Zn fertilization.

5.8 Redox-potential

Zinc deficiency in submerged rice soils is very common owing to the combined effect of increased pH, HCO_3^- and S^{-2} formation (Farooq *et al*., 2018). Flooding initially increases the Zn concentration in soil solution, but will decline with time due to the formation of insoluble compounds such as franklinite, $ZnCO_3$ (Zinc carbonate), $ZnFe_2O_4$ and ZnS (Zinc sulfide) (Sajwan and Lindsay, 1988 & Singh and Abrol, 1986). The formation of these compounds occurs due to the decomposition of soil organic matter.

Formation of insoluble franklinite.

$$Zn^{+2} + 2Fe^{+2} + 4H_2O \xrightarrow{\text{Reduction}} ZnFe_2O_4 \text{ (Franklinite)}$$

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

$$Zn^{+2} + S^{-2} = ZnS \text{ (Sphalerite) in soluble in water}$$

5.9 Soil texture

Coarse/light texture (sandy soils) contains low levels of Zn due to low organic matter status high tendency of erosion. Finer texture (clay soils), which have higher adsorption capacity of organic matter resulting higher CEC values and therefore have highly reactive sites and can retain more Zn than Lighter textured soils (Shukla Mittal, 1979). Consequently, Zn deficiency is more likely to occur in sandy than clayey soils. Clay soils adsorb comparatively more Zn and this adsorption is controlled by CEC and pH (Ellis and Knezek, 1972). While, Reddy *et al.* (Nelson *et al*., 1953) reported that a certain portion of the Zn adsorbed on the clay was not exchangeable but acid soluble, this portion of Zn was not available to the plants. Reddy and Perkin (Reddy and Perkin, 1974) found that kaolonite fixes less Zn than bentonite or illite. Thus clays such as bentonite and

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illite with higher CECs contribute to the fixing of Zn more strongly, thus making it unavailable to plants.

5.10 Nutrient interaction

5.10.1 Phosphorus-Zn interactions

high available phosphate status in soil are one of the most common causes of zinc deficiency in crops by cations added with phosphate salts can inhibit zinc absorption from solution, H^+ ions generated by phosphate salts inhibit zinc absorption from solution and phosphorus enhances the adsorption of zinc into soil constituents. The interaction is usually termed ‘P-induced- Zn deficiency’. It was suspected that formation of an insoluble $Zn_3(PO_4)_2$ in the soil reduced the Zn concentration in soil to deficient levels. But these suspicions were disproved and further observed that Zn3 (PO4)2 was a good source of fertilizer for sorghum (Brown *et al.*, 1970). It was suspected that formation of an insoluble $Zn_3(PO_4)_2$ in the soil reduced the Zn concentration in soil to deficient levels. In general, four possible causes have been considered responsible for P induced- Zn deficiency. These include (i) a P-Zn interaction in soil; (ii) a slower rate of translocation of Zn from the roots to shoot; (iii) a simple dilution effect on Zn concentration in plant tops due to growth responses to P; (iv) a metabolic disorder within plant cells related to an imbalance between P and Zn (Olsen, 1972). While, many researchers have reported that applied P accentuated Zn deficiency symptoms in plants (Loneragan *et al*., 1979 & Sharma *et al*., 1968). The higher P levels in soil reduced the Zn concentrations in the plant tops and also reduced total Zn contents (Singh *et al.*, 1986 & Clark, 1978).

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5.10.2 Nitrogen-Zn interactions

The available of Zinc in soil depend on application of nitrogen fertilizers. The application of N promotes the growth of plants, to a lesser extent in changing the pH of the root environment hence it is possible to find positive interactions between increasing levels of Zn and N fertilizers (Alloway, 2004). It was reported that wheat grown on N deficient soil with adequate levels of all nutrients except N and Zn, did not respond to Zn application in the absence of NH_4NO_3 fertilizer, however, a strong response to Zn application was observed in the presence of N fertilizer (Chaudhry *et al.*, 1970). Several macronutrient elements, including calcium, magnesium, potassium and sodium are known to inhibit the absorption of zinc by plant. Soil-test each field to help identify where crops will respond to Zn. However, in soils low in Zn and high in fertility, N fertilizers have ameliorated (or intensified) Zn deficiency by affecting Zn absorption through changing pH (Viets, 1957).

5.10.3 Copper-Zn interactions

It was reported that Cu and Zn may interact in several ways: Zn strongly depresses Cu absorption, Cu competitively inhibits Zn absorption and Cu nutrition affects the redistribution of Zn within plants (Loneragan and Webb, 1993). A very strong Cu-Zn antagonism has been observed in wheat growing on soils deficient in Cu and Zn (Kausar *et al.*, 1976). Because Zn severely depressed Cu uptake by wheat, Cu did not depress Zn absorption in the same experiment. The reason for the difference in soil and solution culture results may be the form of these ions present in the soil and solution. In solution studies, the Cu and Zn were present as divalent ions whereas in most of the soils they are predominantly present as complex forms and a much higher proportion of Cu is complexed compared to Zn (Geering and Hodson, 1969). So Zn^{2+} activity would be much higher than Cu^{2+} activity at the absorbing sites making it an effective competitor in Cu absorption and making its absorption less sensitive to competition from Cu (Loneragan and Webb, 1993).

5.10.4 Iron-Zn interaction

The interaction between Zn and Fe is also complex like P-Zn interaction. The increased application of Zn had little effect or decreased Fe concentrations in the shoot (Norvell and Welch, 1993 & Safaya, 1976). In the same way, higher levels of Fe generally have only a depressive effect on Zn concentration in plant tissues (Zhang et al., 1991), although it has been shown to increase have no effect on or to decrease the rate of Zn absorption by plant roots. Iron (Fe^{2+}) at low concentrations (10 µM) had no effect on the rate of Zn absorption by wheat seedlings from solutions containing 1 or 10 µM Zn and 50 mM $Ca(NO_3)_2$ (Adriano et al., 1971). But at higher concentrations (100 µM Fe^{2+}), and at concentrations likely to occur in flooded rice soils, Fe completely suppressed the Zn absorption by rice seedlings from a solution of 0.05 µM $ZnCl_2$ with no Ca (Giordano e al., 1974).

5.10.5 C: N ratio

It is proportion to each other: they are carbon and nitrogen, this relationship is called the carbon-nitrogen ratio. Carbon is important because it is an energy-producing factor, and nitrogen, because it builds tissue. C: N ratio increase decomposition of organic matter also increases as well as increase of microorganisms. Therefore, zinc can interrupt the activities in soils, as it negatively influences the activity of microorganisms and earthworms (Suthar and Sing, 2008). This process affects the breakdown of organic matter. Smolders *et al.* (2004) reported the negative effect of zinc toxicity on soil microbial processes, as it hinders the activities of microorganisms.

6. ZINC DEFICIENCY STATUS IN INDIAN SOIL

Zinc deficiency of DTPA- Extractable Zn in Indian soils ranged from 1.96 to 63.3% with an average deficiency of approximately 36.5%. Minimum Zn deficiency negligible in acid soils of north east states whereas more than 50% soils of the states like Tamil Nadu (63.3%), Rajasthan (56.5%), Madhya Pradesh (57.1%) and Goa (55.3%) exhibited Zn deficiency. In the states like Arunachal Pradesh, Himachal Pradesh, Meghalaya, Mizoram, Nagaland, Tripura and Uttarakhand had Zn deficiency in less than 10% of soils. In the states like Punjab, Andhra Pradesh, Chhattisgarh, Telengana, Uttar Pradesh, Assam and Odisha Zn deficiency ranged between 20 to 30% (Figure 8a and 8b) (Shukla and Tiwari, 2016).

7. PERIODIC CHANGES IN LEVEL OF ZINC DEFICIENCY IN INDIAN SOIL

A periodic change of zinc deficiency level in Indian soil was depicted in figure 9a and figure also showed that the Zn deficiency level in the Indian soil declined from 46.0% (1967) to 36.5%

(2017) (Shukla and Behera, 2019). The extensive research and extension activities on micronutrients, especially on Zn by AICRP-MSPE including other agencies in creating awareness among the farmers and initiative taken by the fertilizer industry, led to an increase in Zn fertilizer use linearly. Resultant build-up of Zn level in soil, Zn deficiency decreased to 36.5% in 2017 and based on the current trends, Zn deficiency would reduce to 21% by 2025-30 (Figure 9b) provided the unstinted efforts of fertilizer industry and government support and promotion of Zn fertilization will continue.

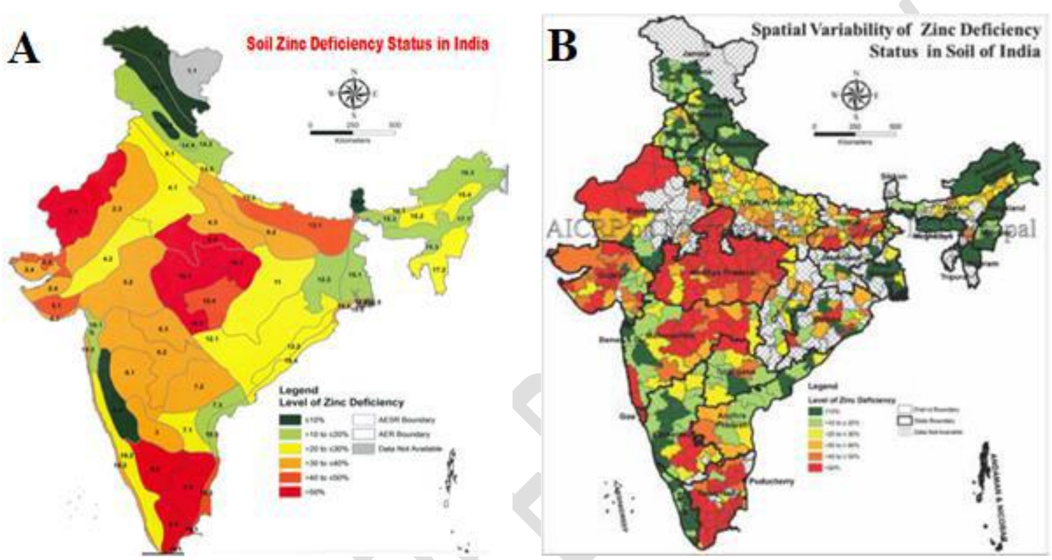


Figure 8a: (A) Agro-ecological sub region wise (B) Kriged Zn deficiency maps of India (***Source:*** Shukla and Tiwari, 2016).

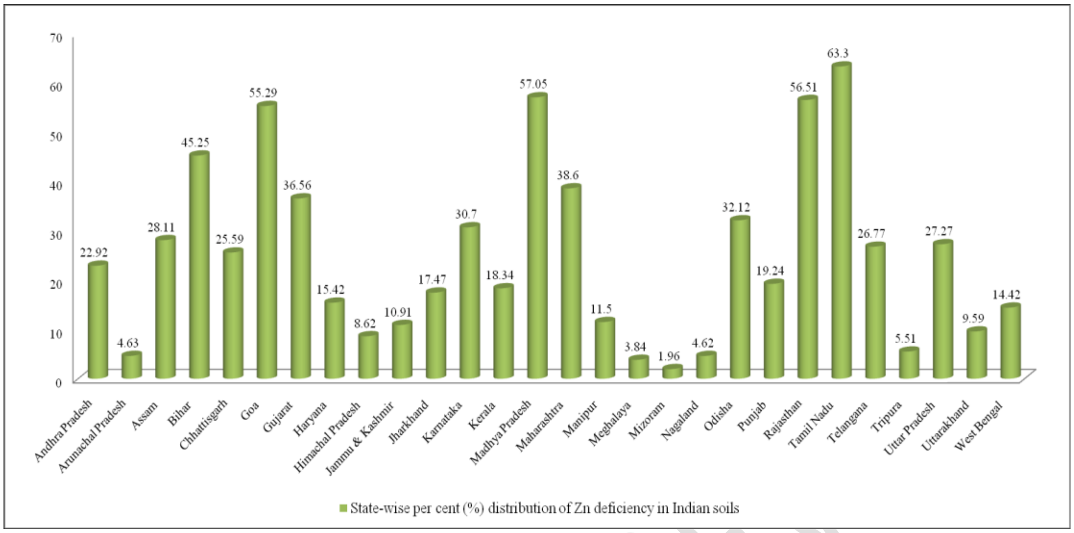


Figure 8c: State-wise per cent (%) distribution of Zn deficiency in Indian soils (***Source:*** Shukla *et al.*, 2018).

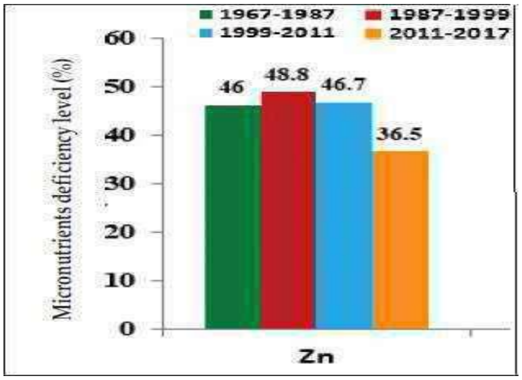


Figure 9a: Periodic changes in the extent of micronutrient deficiencies in Indian soils on time scale [***Source:*** Shukla and Behera (2019)].

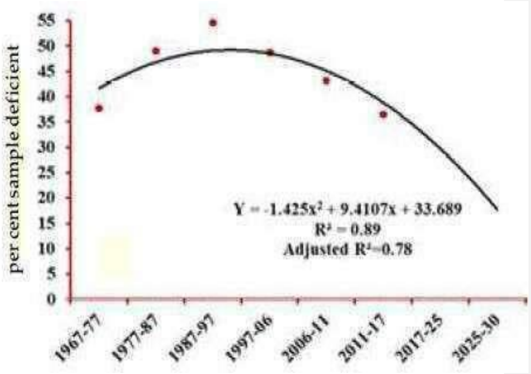


Figure 9b: Prediction of soil Zn deficiency (***Source:*** Shukla et al., 2018)

8. TRANSITION ZONE OF CRITICAL LIMIT FOR ZINC IN SOILS

The range between deficient and toxicity levels of zinc is narrow in soils. Hence, the farmers must be careful in the rate of Zn fertilizer application. Sensitive crops to excess zinc are: corn, bean, sorghum, onions, sweet corn, flax, fruit trees (deciduous), grapes and hops, etc. As per Lindsay and Norvell (1978), 0.6 mg Zn kg^{-1} soil was considered as critical limit. But, with changing status of Zn in Indian soils and crop responses to Zn application, the critical limit generalized "*Transition Zone of Critical Limit*" (Shukla and Tiwari, 2016 and Shukla and Behera, 2018) that is established relation between crop yield response and available Zn content in soil. Because only single value of critical limit (*viz.*, deficiency and sufficiency level) cannot justify the application of fertilizer does especially in where (India) different types of soils are available and farmers are followed different crops in different seasons. Hence they are suggested that the soil fertility rating in the level of deficient and sufficient for available Zn in soils (Figure 10) (Table 2) and in crop plants (Table 3).

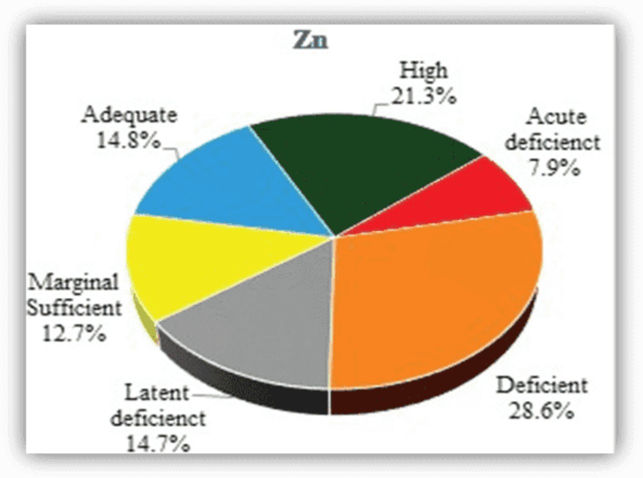


Figure 10: Transition zone of critical limit of Zinc per cent (%) distribution in Indian soil [***Source:*** Shukla and Behera (2019)]

Table 2. Transition zone of critical limit of Zinc (Zn)

Transition zone of critical limit	DTPA-Zn (mg kg^{-1})	Rating
Acute deficiency	≤ 0.3	Deficient
Deficiency	>0.3 to ≤ 0.6	
Marginally deficient	>0.6 to ≤ 0.9	
Marginally sufficient	>0.9 to ≤ 1.2	Sufficient
Adequate	>1.2 to ≤ 1.8	
High	>1.8	

***Sources*:** Shukla and Tiwari (2016)

Table 3. Critical concentration of Zn in different crop plants

Crop	Growth Stage (DAS)	Plantpart	Concentration (mg kg^{-1} plant parts)				
			Deficient	Threshold deficiency	Adequate	Threshold toxicity	Toxic
Cereals							
Wheat	35	ML	<15	20	22	-	-
Barley	35	ML	<15	20			-
Rice	35	ML	<15	20	22-100	100	-
Maize	50	ML	<15	25	28	-	-
Millets							
Sorghum	35	ML	<15	20	22-50	50	-
Pearl millet	44	ML	<20	40	42-100	100	>200
Legumes							
Gram	60	ML	<7	15	17	-	-
Pea	42	ML	<12	20	22-80	80	>300
Lentil	55	ML		10	11-50	50	-

Green Gram	28	ML	<15	20	22	-	-
Black gram	30	ML	<12	25	27-45	45	-
Cowpea	32	ML	<20	45	50-150	150	-
Vegetables							
French bean	75	YL	36	50	60-120	130	180
Oil crops							
Mustard	30	ML	<25	30	33	-	-
Safflower	100	YL	22	27	30-60	62	68
Rapeseed	95	YL	17	22	25-50	52	60
Sunflower	73	L	<20	40	45-100	100	200
Groundnut	45	YL	22	28	30-95	100	115
	100	Seed	12	16	20-30	32	38
ML=Middle leaf; LB=Leaf base; YL=Young leaf; L=Leaf							

Sources**:** Shukla *et al.*, 2016

9. ZINC DEFICIENCY IN SOILS AND CROPS

9.1 Zinc deficiency in soils

Many zinc deficiency problems around the world are associated with sandy soils and calcium carbonate-rich soils. Deficiencies of zinc occur in many parts of the world on a wide range of soil types but semi-arid areas with calcareous soils, tropical regions with highly weathered soils and sandy-textured soils in several different climatic zones tend to be the most seriously affected (Alloway, 2008; Akay, 2011). Zinc deficiency can be seen in eroded, calcareous and weathering acidic soils. Zinc deficiency is often accompanied with iron deficiency in calcareous soils. Zinc deficiency in these soils is related to adsorption of solution zinc in the soil by clay and limestone particles. In eroded soils, zinc deficiency is caused by organic matter deficiency. Also zinc deficiency may be related to weather conditions, zinc deficiency increases in cold and wet weather conditions. It may be due to the limited root growth in cool soils, or reduction activity of microorganisms and reduction the release of zinc from organic materials (Alam *et al.*, 2010; Abdou *et al.*, 2011; Mousavi, 2011). High concentrations of carbonate (HCO_3) prevent of zinc uptake by plants shoot (Gokhan, 2002). Different crops have a difference relative sensitivity of to zinc deficiency (Table 4).

Table 4: Relative sensitivity of crops to zinc deficiency (***Source:*** Alloway, 2008)

High	Medium	Low
Bean	Barley	Alfalfa
Citrus	Cotton	Asparagus
Flax	Lettuce	Carrot
Fruit trees (deciduous)	Potato	Clover
Grapes	Soybean	Grass
Hops	Sudan grass	Oat
Maize (corn)	Sugar beet	Pea
Onions	Table beet	Rye
Pecan nuts	Tomato	Wheat
Rice		

Sorghum
Sweet corn

Zinc deficiency symptoms appear on the young leaves of plants first; because zinc is an immobile element that transferred to younger tissues from older tissue. Areas between nervure in plants are yellow by zinc deficient (Vitosh *et al.*, 1994). In dicot plants internode distance and leaf size will be short and in monocot plants, corn especially, bands comes into the main nervure on both sides of leaves in zinc deficient condition Overall, shoot is more affected than the root growing by zinc deficiency (Boardman and McGuire, 1990; Gokhan, 2002; Mousavi, 2011).

9.2 Zinc deficiency symptoms in crops

Some examples of visual symptoms of zinc deficiency on various crops under field conditions have been depicted in figure 11 and also discuss of deficiency symptoms of various crops as given bellow:

9.2.1 Bean

Zinc-deficient dry edible beans first become light green. When the deficiency is severe, the area between the leaf veins becomes pale green and then yellow near the tips and outer edges. In early stages of deficiency, the leaves are deformed, dwarfed and crumpled. In later stages, they look as if they have been killed by sunscald. On zinc-deficient plants, the terminal blossoms set pods that drop off, delaying maturity.

9.2.2 Maize

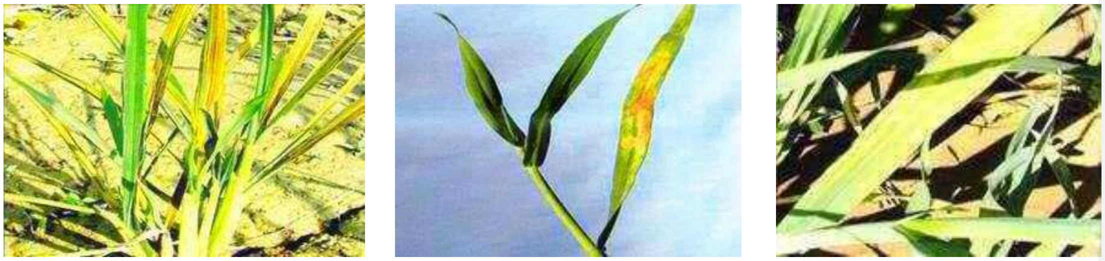
Zinc deficiency in corn appears as a yellow striping of the leaves. Areas of the leaf near the stalk may develop a general white to yellow discoloration. In severe deficiency, the plants have shortened internodes and the lower leaves show a reddish or yellowish streak about one- third of the way from the leaf margin. Plants growing in dark sandy or organic soils usually show brown or purple nodal tissues when the stalk is split. This is particularly noticeable in the lower nodes.

Zn deficiency in Maize

Zn deficiency in Pearl millet

Zn deficiency in Sorghum

Zn deficiency in Bean *Zn deficiency in Bean* *Zn deficiency in Onion*



Zn deficiency in Rice *Zn deficiency in Wheat* *Zn deficiency in Barley*

Zn deficiency in sponge gourd *Zn deficiency in tomato* *Zn deficiency in radish*

Figure 11: Some examples of visual micronutrient deficiency symptoms

9.2.3 Onion

Deficiency in onions shows up as stunting, with marked twisting and bending of yellow- striped tops. In potatoes, early symptoms are similar to leaf roll. The plants are generally more rigid than normal, with smaller than normal leaves and shorter upper internodes.

9.2.4 Pearl millet

Zinc deficiency symptoms in pearmillet plant are appears first on top (younger) leaves. Yellow and white striping spots on upper leaves of stunted plants. Prevent elongation of internodes, which results in crowding of the upper leaves, producing a fan-shaped appearance. The crop lacks vigour and yield poorly.

9.2.5 Sorghum

Zinc deficiency symptoms in sorghum plant are appears first on top (younger) leaves. Dusty brown spots on upper leaves of stunted plants. Uneven plant growth and patches of poorly established hills in the field, but the crop may recover without intervention. Increased spikelet sterility in sorghum, chlorotic midribs, particularly near the leaf base of younger leaves.

9.2.6 Rice

Zinc deficiency symptoms are more common on young or middle-aged leaves. Dusty brown spots appear on upper leaves of stunted plants, sometimes two to four weeks after transplanting, with uneven plant growth and patches of poorly established hills. Under severe deficiency, tillering decreases and time to crop maturity may be increased.

9.2.7 Wheat

Symptoms are followed by the development of whitish-brown necrotic spots on middle- aged leaves. As the severity of zinc deficiency intensifies, the necrotic spots spread on the leaves, and the middle parts of the leaves are often collapsed, showing a "*scorched*" appearance. Maturity is delayed.

10. MANAGEMENTS OF ZINC IN DEFICIENT SOILS

In order to reduce Zn deficiency throughout the susceptible regions, research has been conducted in different states of India that are low in Zn. Apart from this research it was observed that proper management of zinc for sustainable crop production generally depend on mainly five factors (Figure 12) such as:

- Determination of availability of Zn in soil and plant.
- Suitable sources of Zn containing material.
- Definite rate of Zn application.
- Suitable time of Zn application.
- Suitable method of application of Zn containing materials.

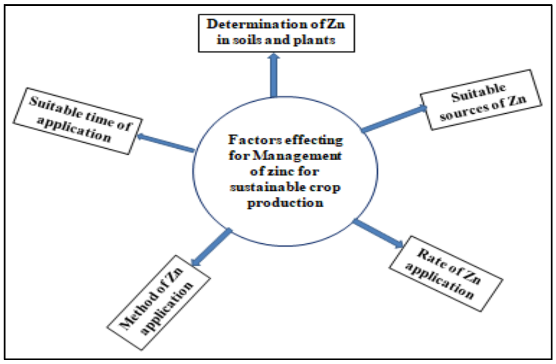


Figure 12 Factors affecting for management of Zinc for sustainable crop production

Comment [L7]: Add References

Determination of available Zn in soils and plants

10.1.1 Method of determination of available Zinc in soils [DTPA extractable Zn (Lindsay and Norvell, 1978)]

Instruments:

i. Mechanical shaker
ii. Atomic absorption spectrophotometer (AAS)

Reagents:

i. *Dilute HCl:* AR grade HCl diluted 5 times with double distilled water.
ii. *DTPA extractant:* Dissolve 1.967 g of AR grade diethyline triamine penta acetic acid (DTPA) and 1.47 g of $CaCl_2.2H_2O$ (AR grade) in about 25 ml of double distilled water followed by add 13.3 ml of Trietanolamine (TEA). Transfer the solution to one litre volumetric flask. Just before making up the volume, adjust pH to 7.3 with dilute HCl. This reagent has 0.005M DTPA, 0.01M $CaCl_2.2H_2O$ and 0.1M Tri ethanol amine.

Procedure:

i. Weigh 10 g of soil sample in 100 ml conical flask
ii. Add 20 ml of the DTPA extractant and shake for 2 hour on a mechanical shaker.
iii. Filter the solution through Whatman No. 1 filter paper
iv. Feed the standard working solutions and prepare a standard curve by plotting AAS reading against the element concentrations.
v. Measure the element concentration in the filtrated solution by using AAS.

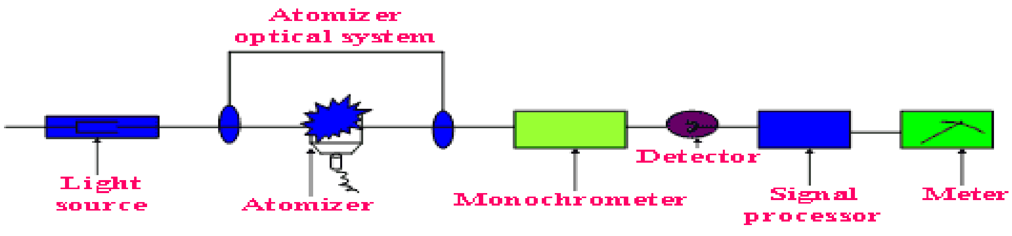


fig .13 Basic component of an atomic absorption spectrophotometer

Preparation of standard curve:

Working standard for Zn

i. Prepare 100 ppm Zn solution by diluting 10 ml of commercially available 1000 ppm standard solution of Zn to 100 ml.
ii. Prepare 10 ppm standard solution by diluting 10 ml of 100 ppm Zn solution to 100 ml.
iii. Prepare working standard solution of 0.5, 1.0, 1.5 and 2.0 ppm by diluting 5, 10,15 and 20 ml of 10 ppm solution to 100 ml.

Precautions:

All the glassware to be used for micronutrient analysis must be clean properly with the help of double distilled water to get better result.

Calculation:

Available DTPA extractable Zn in soil (mg kg^{-1} or ppm) = $(A \times 20)/ 10 = A \times 2$
Where, A = Sample reading in AAS (in ppm)

10.1.2 Determination of Zinc in plants (Piper, 1966)

After the harvesting of plant (Harvest may be different growth stages and different parts of plant) samples were processed with following standard procedure of washing, drying and grinding. Ground material (0.5g) was digested with 10 mL of tri-acid mixture (HNO_3:$HClO_4$:H_2SO_4 in 10:4:1). It was kept in digestion chamber till complete digestion (Piper, 1966). The residue was dissolved in double-distilled water and after filtration (Whatman filter paper No. 42) final volume was made to 25 mL. Zinc content in plant was determined with the help of Atomic Absorption Spectrophotometer (AAS).

Calculation:

Zinc content in plant sample (mg kg^{-1} or ppm) = $[(A \times DF)/ W]$
Where,
A = Sample reading in AAS (in ppm)
DF = Dilution Factors
W = Ground sample weight

10.1.3 Estimation of Zn Use Efficiency

The estimated values of Zn use efficiencies were computed by following the formulas suggested by Fageria (2009) and Shivay and Prasad (2012):

$$\text{Agronomic efficiency (AgE)} = \frac{GY_{Zn} - GY_C}{Zn_a}$$

$$\text{Physiological efficiency (PE)} = \frac{Y_{Zn} - Y_C}{U_{Zn} - U_C}$$

$$\text{Agro} - \text{physiological efficiency (AgPE)} = \frac{GY_{Zn} - GY_C}{U_{Zn} - U_C}$$

$$\text{Apparent recovery efficiency (ARE)} = \frac{U_{Zn} - U_C}{Zn_a}$$

$$\text{Utilization efficiency (UE)} = \text{PE} \times \text{ARE}$$

$$\text{Partial factor productivity (PFP)} = \frac{GY_{Zn}}{Zn_a}$$

Where, GY_{Zn} is the grain yield of Zn treated plots, GY_C is the yield of untreated plots, Zn_a is the total amount of Zn applied, Y_{Zn} is the grain and straw yield of Zn treated plots, Y_C is the grain and straw yield of untreated plots, U_{Zn} is the Zn uptake in grain and straw of Zn treated plots, and U_C is the Zn uptake in grain and straw of untreated plots.

10.2 Suitable sources of different Zn containing Fertilizers

After detecting zinc deficiency, its remedial measure is important for improving the crop productivity in Zn deficient soils. Remedial measures also include suitable sources of Zn containing fertilizers (Table 5).

Table 5: Selected Zn fertilizers and their formula, Zn content, water solubility

Zinc sources	Formula	Zn content (%)	Water solubility
Zinc sulfate heptohydrate	$ZnSO_4.7H_2O$	21	Highly solubility
Zinc sulfate monohydrate	$ZnSO_4.H_2O$	33	Highly solubility
Zinc oxide	ZnO	72-80	Low solubility
Zinc chloride	$ZnCl_2$	50	Highly solubility
Zinc nitrate	$Zn(NO_3)_2.3H_2O$	23	Highly solubility
Zn EDTA	$Na_2ZnEDTA$	8-14	Highly solubility

10.3 Suitable quantity of Zn application

Quantities of Zn requirement generally depend on availability of Zn in soil. Following table 6 clearly showed that the rate of Zn requirement according to their Zn availability of soil.

Table 6: Recommendations of Zn application based on soil Zn fertility status

Transition zone of critical limit	DTPA-Zn (mg kg^{-1})	Recommendation of Zn application in crops and cropping systems
Acute deficiency	≤ 0.3	5.0 kg Zn ha^{-1} basal (25 kg $ZnSO_4.7H_2O$) per crop sequence

Deficiency	>0.3 to ≤ 0.6	5.0 kg Zn ha^{-1} basal (25 kg $ZnSO_4.7H_2O$) in every alternateyear Or 3.0 kg Zn ha^{-1} basal (15 kg $ZnSO_4.7H_2O$) per crop sequence + one foliar spray of 0.1% Zn at critical growth stages
Marginally deficient	>0.6 to ≤ 0.9	2.5 kg Zn ha^{-1} basal (12.5 kg $ZnSO_4.7H_2O$) per crop sequence Or Three foliar spray of 0.1% Zn at critical growth stages
Marginally sufficient	>0.9 to ≤ 1.2	2.0 kg Zn ha^{-1} basal (10 kg $ZnSO_4.7H_2O$) per crop sequence Two foliar spray of 0.05% Zn at critical growth stages
Adequate	>1.2 to ≤ 1.8	Maintenance dose of 1.5 kg Zn ha^{-1} basal (7.5 kg $ZnSO_4.7H_2O$) per two crop sequence
High	>1.8	Not need of Zn application

Source: Shukla and Behera (2018)

Table 7 Requirement of Zn containing fertilizers for different doses of Basal and foliar application

Zn containing fertilizers	Basal application of Zn				
	5 kg Zn	2.5 kg Zn	2.0 kg Zn	1.5 kg Zn	1.0 kg Zn
	Zn fertilizer is required in kg				
Zinc sulfate heptohydrate	23.81	11.90	9.52	7.14	4.76
Zinc sulfate monohydrate	15.15	7.58	6.06	4.55	3.03
Zinc oxide	6.25-6.95	3.13-3.48	2.50-2.78	1.88-2.09	1.25-1.39
Zinc chloride	10.00	5.00	4.00	3.00	2.0
Zinc nitrate	21.75	10.88	8.70	6.53	4.35
Zn EDTA	35.70-62.50	17.85-31.25	14.28-25.00	10.71-18.75	7.14-12.50

Table 8 Requirement of Zn containing fertilizers for different doses of Basal and foliar application

Zn containing fertilizers	Foliar application of Zn	
	0.1% Zn	0.05% Zn
	Zn fertilizer is required in g per liter	
Zinc sulfate heptohydrate	4.76	2.38
Zinc sulfate monohydrate	3.03	1.52
Zinc oxide	1.25-1.39	0.63-0.70
Zinc chloride	2.0	1.00
Zinc nitrate	4.35	2.18
Zn EDTA	7.14-12.50	3.57-6.25

Suitable Time of Zn application

Time of zinc application mainly depends upon its content in seed or severity of its deficiency.

Best time of zinc addition is prior to sowing or transplanting of crops because maximum zinc absorption by plants takes place upto tillering or preflowering stages. Split application of zinc sulphate in rice is recommended as 50% at the time of sowing or transplanting and remaining 50% before or upto tillering stage. Basal application of zinc to soil isfound the best. However, if it is missed, zinc deficiency can be corrected by top dressing of zinc upto 45 days. Foliar sprays of 0.5% zinc sulphate three to four times at 7-10 days interval just after 21 days sowing or transplanting of crops for control zinc deficiency more efficient and effectively. If deficiency persists then continue more sprays.

10.5 Method of Zn application

Basal application of Zn to soil through broadcast and mixed or its band placement below the seed proved superior to top dressing, side dressing or band placement, foliar sprays or soaking or coating of seeds/ seedling in Zn solution/ slurry and foliar application of crops.

10.5.1 Soil application

In highly Zn deficient soils, basal application of Zn containing fertilizers give the superior improve of soil. Generally application of zinc varies with their soil type and it ranged from 0.5 to 5.0 kg per hectare (Table 5). Kumar *et al.*, 2018 reported that the high deficiency of Zn in soil can also be effectively controlled with 5.0 and 7.5 kg Zn per hectare on hybrid rice crops.

10.5.2 Foliar application

Foliar sprays of zinc sulphate at 0. 5 to 2.0 % is very effective for both annul and perennial crops. Singh, 2008 reported that Deficiency of Zn can also be effectively controlled with 2 to 4 spray of 0.5% zinc sulphate salt solution on standing crops. Sometimes only Zn @ 0.05 to 0.1 %, two-three foliar spray should be applied at critical growth stages of crops.

10.5.3 Seed treatment

Seed treatment with Zn fertilizers also give equally improve as that of its foliar sprays or soil application. Seed treatment with Teprosyn ZnP (Liquid) at the recommended level 8 ml kg^{-1} seed and Seed treatment with zinc sulphate ($ZnSO_4.7H_2O$: 33% Zn) at the rate of 5.0 mg Zn kg^{-1} seed superior improve of crops. Adhikari *et al.*, 2015 reported that the zinc seed treatments significantly improved leg- hemoglobin contents, nodulation, grain yield, grain Zn yield, grain bio-available Zn, grain minerals and grain Zn concentration compared with control treatments in both desi and kabuli chickpea.

10.5.4 Nano-coating of zinc

Seed coating of Zn materials like concentrated Zn: zinc phosphate was found good in correcting Zn deficiency in bold size seed crops in marginally deficient soils. seed coating with ZnO both microns scale (<3 µm) and nano-scale (<100 nm), ZnO powder at 25 mg Zn g^{-1} seed and at 50 mg Zn g^{-1} seed showed the improved on growth and development of several crops *i.e.*, maize

(*Zea mays* L.), soybean (*Glycine max* L.), pigeon pea (*Cajanas cajan* L.) and ladies finger (*Abelmoschus esculentus* L.) (Ullah *et al*., 2020).

11. ZINC TOXICITY

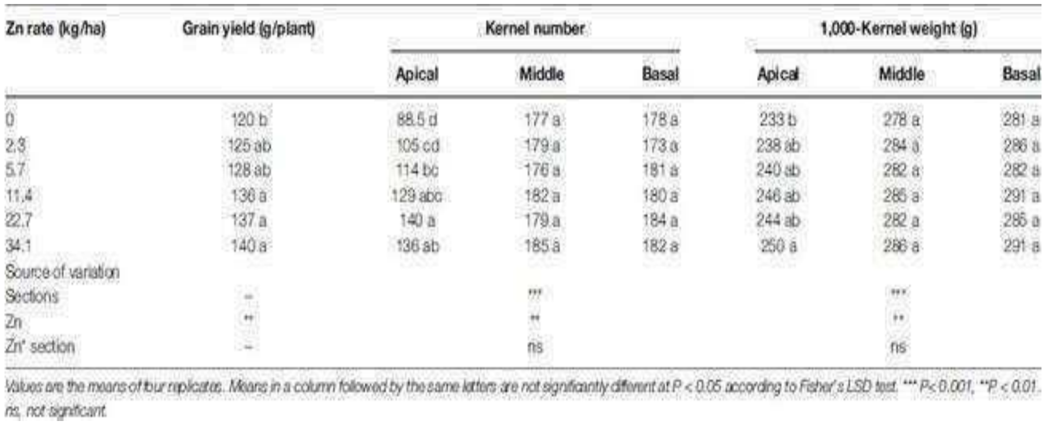
No doubt, Zn has got a position as an essential micronutrient for plants, but Zn toxicity is more harmful than its deficiency. Zn has a special place among the trace metals, unlike Fe, Mn, Cu, Ni and several other metals that are not the components of plant enzymes since Zn is a constituent of carbonic anhydrase and small quantities of Zn are essential for some plant species. When zinc amount is excessive, causes toxicity in plants. Leaf and root growth and development decreased by zinc toxicity. Production of NADPH in plant chloroplasts are decreases with increasing zinc concentration. In addition, production of free radicals will increases in plants. Activity of RUBP carboxylase enzyme and Photosystem II decreases by zinc toxicity. Zinc toxicity reduces ATP synthesis and chloroplasts activity and photosynthesis will decline as a result. Also, large amounts of zinc reduces uptake of P and Fe. The critical toxicity concentrations in leaves of crop plants range from 100 μg Zn g^{-1} dw (Ruano *et al*., 1988) to more than 300 μg Zn g^{-1}. Resistance to zinc is differences in various plants, the plants such as beans, corn, onions, sorghum, rice, citrus fruits and grapes have most sensitivity to zinc deficiency, barley, lettuce, potatoes, soybeans, sugar beet and tomato have moderate sensitivity to zinc deficiency and carrots, alfalfa, asparagus, radish, and forage plants are resistance to zinc deficiency (Vitosh *et al*., 1994).

12. RESPONSE OF CROPS TO ZINC APPLICATION (SOME REVIEW REPORTS)

12.1 Grain Yield, Kernel Number, and Kernel Weight in Three Sections of Maize Spikes

Liu *et al*., 2020 reported that the zinc application on maize grain yield was increased significantly from 4.2 to 16.7% compared with no Zn application (Table 9). Both KN (Kernel number) and TKW (1000 kernel weight) in the apical sections of maize spikes were increased significantly with the amount of Zn applied levels, while the KN and TKW of the middle and basal sections were not significantly affected (Table 9). Compared with no Zn application, the KN and TKW of the apical section of maize spikes increased from 19.3 to 54.5% and 2.14 to 7.30%, respectively. Both KN and TKW of the apical section of maize spikes were lower than those of the middle and basal sections (Table 9).

Table 9: Effects of Zn various application rates on grain yield, kernel number per spike, and1000-kernel weight of the apical, middle, and basal sections of maize spikes under field conditions.



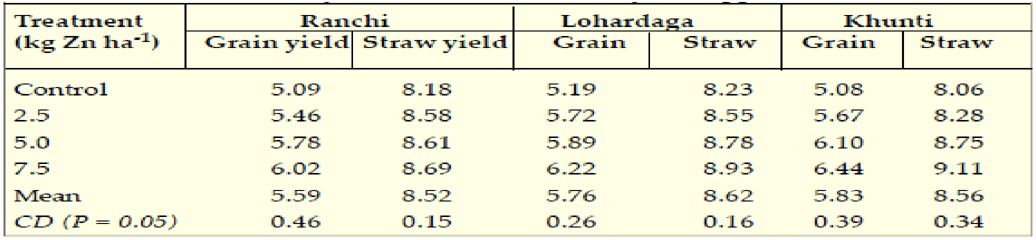
Zn rate (kg/ha)	Grain yield (g/plant)	Kernel number			1,000-Kernel weight (g)		
		Apical	Middle	Basal	Apical	Middle	Basal
0	120 b	88.5 d	177 a	178 a	233 b	278 a	281 a
2.3	125 ab	105 cd	179 a	173 a	238 ab	284 a	286 a
5.7	128 ab	114 bc	176 a	181 a	240 ab	282 a	282 a
11.4	136 a	129 abc	182 a	180 a	246 ab	285 a	291 a
22.7	137 a	140 a	179 a	184 a	244 ab	282 a	285 a
34.1	140 a	136 ab	185 a	182 a	250 a	286 a	291 a
Source of variation							
Sections	–		***			***	
Zn	**		**			**	
Zn* section	–		ns			ns	

*Values are the means of four replicates. Means in a column followed by the same letters are not significantly different at P < 0.05 according to Fisher's LSD test. *** P< 0.001, **P < 0.01. ns, not significant.*

12.2 Yield of Hybrid Rice as Influenced by Zinc Application

Kumar *et al.*, 2018 also reported that the zinc application significantly influenced the grain yield of hybrid rice at all the three locations of Jharkhand state (Table 10). At Ranchi, yields obtained at both 5.0 and 7.5 kg Zn ha^{-1} were on par, but were significantly superior to no-zinc treatment. Per cent grain yield response was 13.56 and 18.31 at 5.0 and 7.5 kg Zn ha^{-1}, respectively compared to its non-application. At Khunti, grain yield of rice increased with graded levels of applied zinc. Response to Zn application was highest at 7.5 kg Zn ha^{-1}, which was 26.81% higher than the control. At Lohardaga, the grain yield in no zinc plot was 5.19 t ha^{-1}. This increased to 6.22 t ha^{-1} with application of 7.5 kg Zn ha^{-1}. Per cent response to Zn application in grain yield of hybrid rice varied from 10.23 to 19.26 with soil application of 2.5 to 7.5 kg Zn ha^{-1} (Figure 14).

Table 10: Yield (t ha^{-1}) of hybrid rice as influenced by zinc application



Treatment (kg Zn ha^{-1})	Ranchi		Lohardaga		Khunti	
	Grain yield	Straw yield	Grain	Straw	Grain	Straw
Control	5.09	8.18	5.19	8.23	5.08	8.06
2.5	5.46	8.58	5.72	8.55	5.67	8.28
5.0	5.78	8.61	5.89	8.78	6.10	8.75
7.5	6.02	8.69	6.22	8.93	6.44	9.11
Mean	5.59	8.52	5.76	8.62	5.83	8.56
CD (P = 0.05)	0.46	0.15	0.26	0.16	0.39	0.34

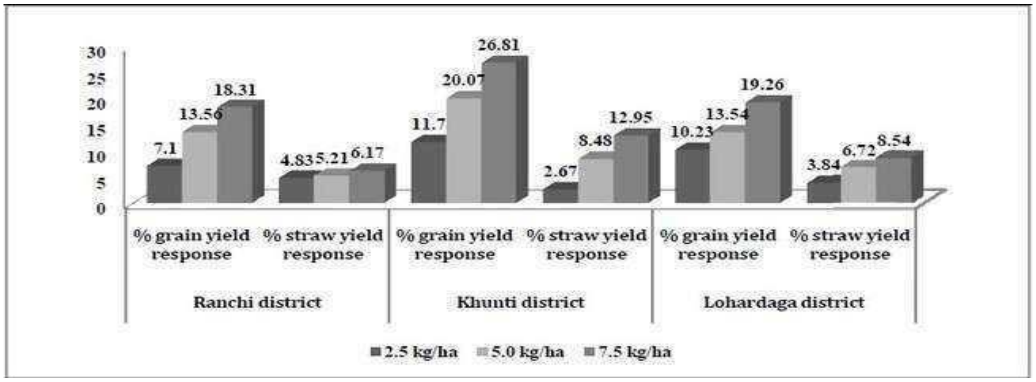
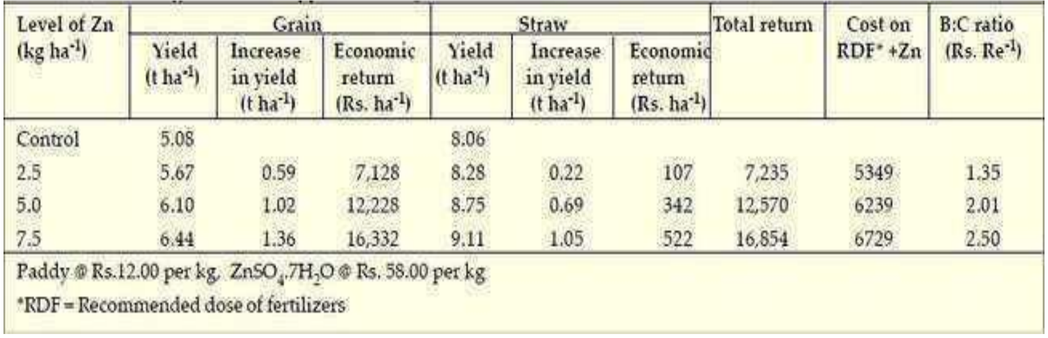


Figure 14: Per cent yield response to Zn application in hybrid rice

12.3 Economic Gains in Hybrid Rice Cultivation from Use of Zinc Fertilizer

Zinc use in hybrid rice over and above the recommended N, P and K fertilizers could help farmers in getting higher monetary gains (Table 11). Gains were higher with application of 7.5 kg Zn ha^{-1} compared to 5.0 and 2.5 kg ha^{-1} rates of Zn application. The benefit:cost ratio of Zn application (Rs. Re^{-1}) in hybrid rice was 2.01 and 2.50 under 5.0 and 7.5 kg Zn ha^{-1} rate which suggests that Zn application is a profitable venture for the farmers. The additional benefit, which probably is still more important, is that of protecting human beings and animals from dietary deficiency of zinc.

Table 11: Economic gain with zinc application in hybrid rice



Level of Zn (kg ha^{-1})	Grain			Straw			Total return	Cost on RDF* +Zn	B:C ratio (Rs. Re^{-1})
	Yield (t ha^{-1})	Increase in yield (t ha^{-1})	Economic return (Rs. ha^{-1})	Yield (t ha^{-1})	Increase in yield (t ha^{-1})	Economic return (Rs. ha^{-1})			
Control	5.08			8.06					
2.5	5.67	0.59	7,128	8.28	0.22	107	7,235	5349	1.35
5.0	6.10	1.02	12,228	8.75	0.69	342	12,570	6239	2.01
7.5	6.44	1.36	16,332	9.11	1.05	522	16,854	6729	2.50

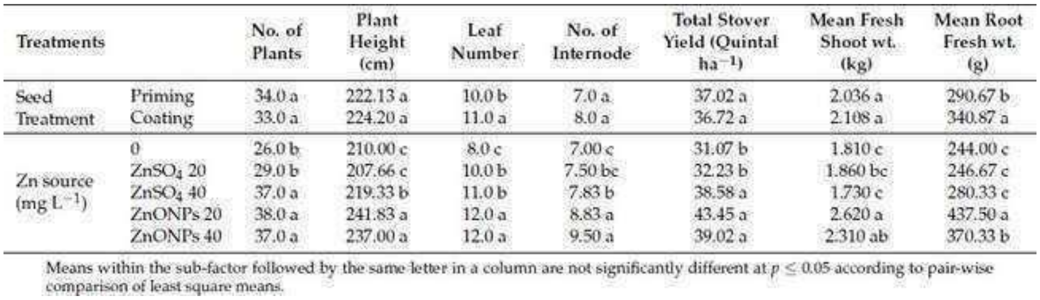
Paddy @ Rs.12.00 per kg, $ZnSO_4.7H_2O$ @ Rs. 58.00 per kg

*RDF = Recommended dose of fertilizers

12.4 Effect of seed treatments with different concentrations of ZnONPs (nano-zinc oxide particles) on vegetative and yield attributing parameters of fodder maize crop grown under field conditions

Nano-zinc fertilizers also essential for plant nutrients, have the potential to improve nutrient use efficiency and productivity of field crops in Zn deficient soils. Tondey *et al.*, 2021 reported that the higher imptovement in vegetative growth and yield parameters (*i.e.*, number of plants, plant height, leaf number, number of internode, stover yield and plant biomass) were showed in treatment of seeds with ZnONPs as compared to bulk $ZnSO_4$ and control treatments was observed (Table 12).

Table 12: Effect of seed treatments with different concentrations of ZnONPs on vegetative and yield attributing parameters of fodder maize crop (variety J-1006) grown under field conditions



Treatments		No. of Plants	Plant Height (cm)	Leaf Number	No. of Internode	Total Stover Yield (Quintal ha^{-1})	Mean Fresh Shoot wt. (kg)	Mean Root Fresh wt. (g)
Seed Treatment	Priming	34.0 a	222.13 a	10.0 b	7.0 a	37.02 a	2.036 a	290.67 b
	Coating	33.0 a	224.20 a	11.0 a	8.0 a	36.72 a	2.108 a	340.87 a
Zn source (mg L^{-1})	0	26.0 b	210.00 c	8.0 c	7.00 c	31.07 b	1.810 c	244.00 c
	ZnSO$_4$ 20	29.0 b	207.66 c	10.0 b	7.50 bc	32.23 b	1.860 bc	246.67 c
	ZnSO$_4$ 40	37.0 a	219.33 b	11.0 b	7.83 b	38.58 a	1.730 c	280.33 c
	ZnONPs 20	38.0 a	241.83 a	12.0 a	8.83 a	43.45 a	2.620 a	437.50 a
	ZnONPs 40	37.0 a	237.00 a	12.0 a	9.50 a	39.02 a	2.310 ab	370.33 b

Means within the sub-factor followed by the same letter in a column are not significantly different at $p \leq 0.05$ according to pair-wise comparison of least square means.

13. CONCLUSIONS

Comment [L8]: It's conclusion not conclusions

Zn impacts not only for plant growth and function but also human nutrition since plants are a dominant part of diets. Our understanding of the impact of Zn in soils and plants, and continues to advance in management of Zn-deficient soils that can improve production and quality of crops. Prevention or correction of Zn deficiency in crops on Zn-deficient soils have a dramatic effect on yield and improve quality of many crops including maize, wheat, rice, onion, bean, sorghum *etc*. While, suitable source, rate of application, time and method of Zn fertilizer application and proper balancing of Zn with other nutrients in soil affect crop yield on Zn-deficient soils. Both soil and foliar application methods of Zn are effective in improving crop yield, produce quality, concentration and uptake of Zn and economic returns. There is a need for more research that ensures adequate and correct use of zinc in crop and side by side encourage to farmers with proven and practical information directly or through farm advisory services, soil and plant testing laboratories, training programme, mass media and other sources.

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Comment [L9]: Cross check all the references with the text references.

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