***Review Article***

# ~~Evaluating the~~ Agronomic Effectiveness of Zinc Sources as Micronutrient Fertilizers: A Comprehensive Review


## Abstract

Zinc occurs naturally in the earth's crust as a part of rocks and in ore minerals. The average concentration of Zn in the lithosphere is 80 mg $kg^{-1}$, which is relatively immobile in soil but moderately mobile in plant. Zinc is ~~essential~~ vital micronutrient for both humans and animals. In plants, Zn plays a vital role as a catalytical, structural and regulatory cofactor of many enzyme reactions. Zinc is necessary for the metabolism of carbohydrates, protein synthesis, the biosynthesis of growth hormones, in particular of indoleacetic acid and the maintenance of the integrity of cell membranes. Zinc deficiency in plants and humans is a widespread problem in many regions of the world. The application of both soil and foliar Zn fertilizers has been used to correct Zn deficiency and to enhance plant Zn nutrition and yields. The agronomic effectiveness of Zn fertilizers has been related to the management factors such as placement, source type, seed treatment, foliar spray and biofortification that can affect the effectiveness of Zn fertilizers.



**Keywords:** Zinc, Biofortification, Seed treatment, Carbohydrates, Protein.




## Introduction

Earth is composed of four main layers, starting with an inner core at the planet's centre, enveloped by the outer core, mantle and crust. The inner core is a solid sphere made of iron and nickel metals about 759 miles (1,221 km) in radius. There the temperature is as high as 9,800 degrees Fahrenheit (5,400 degrees Celsius). Surrounding the inner core is the outer core. This layer is about 1,400 miles (2,300 km) thick, made of iron and nickel fluids. In between the outer core and crust is the mantle, the thickest layer. This hot, viscous mixture of molten rock is about 1,800 miles (2,900 km) thick and has the consistency of caramel. The outermost layer, Earth's crust, goes about 19 miles (30 km) deep on average on land. At the bottom of the ocean, the crust is thinner and extends about 3 miles (5 km) from the seafloor to the top of the mantle.

The average chemical composition of the earth's crust has been determined from tens of thousands of chemical analyses of rocks and minerals taken from the surface or drill holes. The most common elements in the crust by weight are oxygen is most dominant element in earth crust (46.6 %) followed by silicon (27.7 %), these two are non-metals constitute about 74.3 per cent. where aluminum is the most dominant metal in the earth crust (8.1 %) followed by iron (5.0 %), calcium (3.6 %), sodium (2.8 %), potassium (2.6 %) and magnesium (2.1 %). These are all metals constitute about 25.7 per cent eight elements account for about 98.5 per cent of the weight of the crust. And others constitute about 1.41 per cent in which zinc constitute about 0.007 per cent.

**Zinc in soil**

Zinc occurs naturally in the earth's crust as a part of rocks and in ore minerals. The average concentration of Zn in the lithosphere is 80 mg $kg^{-1}$ (Lindsay [17]). The concentration of Zn in soil-forming rocks is very variable. Basaltic igneous rocks generally have a high concentration of Zinc (48–240 mg $kg^{-1}$); whereas silica-rich igneous rocks like granite and gneiss have much lower Zinc content (5–140 mg $kg^{-1}$). In the group of sedimentary rocks, black shales have the highest Zinc content (34–1500 mg $kg^{-1}$), followed by shales and clays (18–180 mg $kg^{-1}$) and sandstone (2–41 mg $kg^{-1}$) reported by Nagajyoti et al. [26].

**General characters of Zinc**

The atomic number of zinc is 30 and molecular weight is 65.38, Zn is a heavy metal whose specific gravity/density is 7.13 g $cm^{-3}$ and the element is called as heavy metal when the gravity/density is more than 5 g $cm^{-3}$ and atomic number is more than 20.

- Plant absorb zinc mainly $Zn^{2+}$
- Relatively immobile in soil but moderately mobile in plant
- Deficiency symptoms mostly appear first on the 2$^{nd}$ or 3$^{rd}$ fully matured leaves from the top of the plant
- Essentiality of Zn was discovered by- A.L. Sommer and C.P. Lipman
- In plant Zn content varies from 25 ppm to 100 ppm
- In soil critical limit of Zn – 0.6 ppm

**Forms of Zinc in soils**

1. **Primary minerals:** Zinc exist as Zinc sulphides, Zinc carbonates and Zinc silicates, Sphalarite- ZnS, Smithsonite- $ZnCO_3$, Willemite-$ZnSiO_4$, Franklinite- $ZnFe_2O_4$ on Weathering Zn ion released into soil solution.
2. **Water soluble zinc:** In soil solution Zn exists as Zn ion and $Zn(OH)^+$ so plant can easily absorb the ionic form of zinc which helps for the better growth and development.
3. **Organically bound zinc:** Zinc form stable complex with organic colloids. This form is not readily available to plants (Luxton et al. [18]).
4. **Exchangeable zinc:** Zinc which adsorbed on charged soil particles later which exchange with other ions present in the soil solution and made available for the plant uptake.
5. **Sorbed and insoluble metallic oxides:** Zn is adsorbed on the surface of clays, oxide minerals, carbonates and organic matters. Which is not available to the crop plant for the growth and development.

**Emerging deficiencies of micronutrients in Indian soils**

Most of the Indian soils are deficient in major nutrient nitrogen and micronutrient zinc, where deficiency of nitrogen was reported in 1950 and zinc was in 1965. And it is estimated that more than 11 essential elements will going to deficit by 2050.

**Zinc deficiency status - world scenario**

Zinc deficiency in agricultural soils is considered to be the most geographically widespread micronutrient deficiency constraint limiting crop production. In a global study carried out in 30 countries by the Food and Agriculture Organization of the United Nations (FAO) to assess the micro- nutrient status of soils, it was estimated that approximately 30 per cent of the world's agricultural soils are Zn deficient. Countries with extensive Zn-deficient areas include China, India, Iran, Pakistan and Turkey where it has been estimated that between 50 per cent and 70 per cent of the cultivated land is affected by Zn deficiency reported by Alloway [1]. Zinc deficiency has been also documented in Western and South-eastern Australia and Brazil.

**Zinc deficiency status in Indian Sub-continents**

The average level of zinc deficiency in Indian soils is 50 per cent and is projected to increase up to 63 per cent by 2025. And the average level of zinc deficiency in Karnataka soils is 56-60 per cent. Soils in which Zn deficiency may occur are Alkaline soil, calcareous soil, leached acidic coarse textured sandy soil, peat or muck soils (organic soils) and some of the

Farming practices that may causes Zn deficiency are application of high dose of phosphatic fertilizer and over liming of acid soils.

**Zinc deficiency symptoms**

**Chlorosis**- yellowing of leaves; often interveinal; in some species, young leaves are the most affected, but in others both old and new leaves are chlorotic.

**Necrotic spots** - death of leaf tissue on areas of chlorosis.

**Bronzing of leaves** - chlorotic areas may turn bronze coloured.

**Rosetting of leaves** - zinc-deficient dicotyledons often have shortened, internodes so leaves are clustered on the stem.

**Stunting of plants** - small plants may occur as result of reduced growth or because of reduced internode elongation.

**Dwarf leaves ('little leaf')** - small leaves that often show chlorosis, necrotic spots or bronzing.

**Malformed leaves** - leaves are often narrower or have wavy margins (Brennan et al. [3]).

**Factors affecting zinc availability**

- **Soil pH and liming** - Availability decreases with increasing in pH. Solubility is pH dependent. Each unit increase in pH = 100-fold decrease in solubility. Deficiency usually occurs on soil pH 6.0 or above. pH <7.7= $Zn^{2+}$, pH >7.7= Zn(OH)+ pH > 9.1= $Zn(OH)_2$.
- **Zinc content in soil -** Soils of Low Zinc Content like Sandy soils, Peats and mucks (Histosols) and High rainfall areas.
- **Root zone depth –** Restricted root zone due to Hardpans, high water tables and soil compaction by tractor
- **Soil type -** Calcareous Soils in which pH is generally 7.4 or higher so deficiency most prevalent. Directly sorbed into carbonates and forms insoluble calcium zincate. Effects of $CaCO_3$ on Zn availability is 3-fold.
- **Organic matter -** Low organic matter content with Incorporation of rapidly decomposable organic matter. Root exudates can chelate Zn. Alkaline soil- Zn is strongly adsorbed by insoluble organic matter. Some microorganisms release zinc from insoluble sources.
- **Soil temperature and microbial activity -** Cool soil temperatures and reduced microbial activity due to this the root system are not well established.
- **Plant species and varieties -** Plants differ widely in their ability to obtain zinc from soils and Availability differs among the varieties.

- **Level of phosphorus -** High level of available P induces Zn deficiency. Application of superphosphate with zinc fertilizer reduced the effectiveness of the zinc. Lime causes more fixation than that caused by P fertilizers.
- **Effect of stress -** Plants are more susceptible to low Zn supply when exposed to heat and drought stress.

**Role of zinc in plant system**

- **Zinc is constituent of enzyme -** Zinc is a cofactor for the enzyme carbonic anhydrase which is essential to carbon uptake during photosynthesis. While important for phytoplankton in terms of photosynthesis, zinc concentrations above 0.05 mg $l^{-1}$ are often considered toxic and impair photosynthesis. Zinc plays an important role in the structure and function of many enzymes, including alcohol dehydrogenases (ADHs) of the MDR type (medium chain dehydrogenases/reductases). Active site zinc participates in catalytic events, and structural site zinc maintains structural stability. Superoxide dismutases (SODs) are universal enzymes of organisms that live in the presence of oxygen. They catalyze the conversion of superoxide into oxygen and hydrogen peroxide reported by Broadley et al. [4].
- **Protein metabolism -** Co-factor of a large number of enzymes involved in "protein synthesis and also involved in stability and functioning of genetic material.
- **Carbohydrate metabolism**
- **Photosynthesis-** Constituent of Carbonic anhydrase (CA) enzyme, which have role in $CO_2$ fixation. CA contains a single Zn atom which catalysis the hydration of $CO_2$.
- **Sucrose and Starch Formation-** Component of aldolase which involved in sucrose formation coupled with important role in starch metabolism.
- **Detoxification of super oxide radicals -** Zn involved in the 2 enzyme Cu-Zn-SOD (most abundant SOD in plant).
- **Anaerobic root respiration -** Carbonic anhydrase is involved in root respiration and Zn is a part of it.
- **Membrane integrity -** Structural orientation of macromolecules and maintenance of ion transport systems.
- **Auxin metabolism -** Required for synthesis of auxin, while reduction in Zn reduces the level of auxins in plants.
- **Uptake and Stress -** Water uptake and transport in plants and alleviate short prairies of heat and salt stress.

- **Synthesis of cytochrome C -** Cytochrome C is primarily known for its function in the mitochondria as a key participant in the life-supporting function of ATP synthesis.

**Types of Zinc Fertilizers**

**A. Inorganic Compounds**

- Include ZnO, $ZnCO_3$, $ZnSO_4$, $Zn(NO_3)_2$ and $ZnCl_2$
- ZnO: nearly insoluble in water but soluble in acids
- $ZnSO_4.7H_20$: heptahydrate form most commonly used

**B. Synthetic Chelates**

- Zn salts + citrates / lignosulphonates / phenols / polyflavonoids
- Cheaper and environment friendly
- Less effective (Karak et al. [14]).

**C. Natural organic complexes**

- Chelating agent (EDTA/DTPA) + metal ion
- Lesser chances of retention by soil colloids, higher transportation from soil to roots
- $Na_2$Zn-EDTA-most commonly used
- Suitable for mixing with conc. fertilizer solutions for soil fertigation and hydroponic application (Mortvedt and Gilkes [24]).

**Agronomic effectiveness of zinc fertilizers**

The agronomic effectiveness of a micronutrient source is defined as the degree of crop response per unit of applied micronutrient. From the perspective of a fertilizer technologist, an effective fertilizer is the one that gives the maximum plant response at the lowest application cost. The agronomic effectiveness of Zn fertilizers has been mainly related to the water solubility of the Zn source, though other management factors such as placement and source type can affect the efficiency of uptake of Zn from soil-applied fertilizers reported by Gangloff et al. [10].

**Biofortification of zinc**

Biofortification is the process that aims to increase the concentration of nutrients in edible portions of crop plants either through fertilization (agronomic biofortification) or plant breeding (genetic biofortification) given by White [45]. Biofortification could provide a range of certain micronutrients for people who don't have access to other interventions. As staple foods are comparatively cheap and accessible to the majority of people, the biofortification of staple crops is a primary target. Although the efficiency of biofortification is not comparable to food supplementation, it can still help reduce the micronutrient intake gap and increase the daily intake of vitamins and minerals throughout a person's life and this may have significant impact on human health by reducing malnutrition reported by Cakmak [5]. Mishra et al. [22] reported that significantly higher Zn content (23.61 mg $kg^{-1}$) in Phule Maulee variety of sorghum. They also reported significantly higher grain yield (4.82 t $ha^{-1}$) in recommended dose of fertilizer + $ZnSO_4$ (soil applied 30 kg $ha^{-1}$) + $FeSO_4$ (soil applied 30 kg $ha^{-1}$) + foliar application of $ZnSO_4$ (0.50 %) and $FeSO_4$ (0.10 %) due to the plant uptake zinc in its oxidized forms, $Zn^{2+}$ form, plants use various zinc uptake mechanisms. One of these is the chelation mechanism – the plant releases compounds called siderophores which bind zinc and enhance its solubility. This mechanism also involves bacteria. Another mechanism involves the release of protons ($H^+$) and reductants by the plant roots to lower pH levels in root zone. The result is increased zinc solubility and availability. Meena and Fatima [21] reported that application of $ZnSO_4$ at 0.2 per cent and $FeSO_4$ at 0.1 per cent as seed treatment + foliar spray of $ZnSO_4$ at 0.5 per cent and $FeSO_4$ at 0.5 per cent at panicle initiation and boot leaf stage produces a greater number of productive tillers per hill, Panicle length. number of grains panicle $^{-1}$ and grain yield in hybrid rice. This might be due to zinc and iron are essential for several enzyme systems that regulate various metabolic activities in plants and photosynthesis, resulting in increased plant height and other growth and yield parameters. Zinc activates enzymes that are responsible for the synthesis of certain proteins. It is used in the formation of chlorophyll and some carbohydrates and is used in the conversion of starches to sugars. Zinc also helps plant tissue withstand cold temperatures.

Application of RDF + Basal application of Zn EDTA @ 20 kg $ha^{-1}$ gives higher grain yield in pearl millet. This increase in yield might be due to increase in biomass, enhancement in photosynthesis and higher translocation of photosynthates towards grain which ultimately increased the yield of plant reported by Panda et al. [29]. The fresh cob and fodder yield increased due to improved availability of micronutrients (Zn and Fe) which could be attributed to the formation of stable organometallic complexes of micronutrients with organic matter, especially during the enrichment process to last for a longer time and release of nutrients slowly in the soil system in such a way that the nutrients are protected from fixation and made available to the plant root system throughout the cropping period and higher accumulation of photosynthates and better translocation of photosynthates from source and sink which ultimately higher productivity of crops reported by Srivastav et al. [42], Anilkumar and Kubsad [2] and Fakeerappa and Hulihalli [8].

The increase in protein content by zinc fortification ascribed due to the role of Zn in nitrogen metabolism and protein synthesis. The enzyme activities of nitrite reductase, nitrate reductase and glutamine synthetase increased and the free $NO_3^-$ concentration decreased, but the soluble protein concentration increased significantly in the shoots after Zn supply reported by Choudhary et al. [6].

**Zinc fertilizer effectiveness in Soil**

The application of ZnEDTA were mixed at a rate of 4 mg Zn $kg^{-1}$ soil was recorded higher dry matter in seed and tops and higher Zn concentration in seed and tops in navy bean due to the chelated form of Zinc is not susceptible to this fixation as the chelating compound such as EDTA (Ethylenediamine Tetra acetic Acid) bonds itself to Zinc in a claw-like fashion to prevent the phosphate from binding with the Zinc and therefore enhancing the bioavailability of the Zinc reported by Morghan [23] and Goos et al. [11].

The application of zinc at 30-60 cm depth recorded higher shoot dry weight and Shoot/root ratio where application of zinc at 10-15 cm depth recorded higher root dry weight and Surface area in maize as due to Zn application increased the production and activity of indole-3-acetic acid, which promotes root growth. These observations occurred at flowering stage when the tips of brace root may be just rooted in 25–30 cm depth and root system of modern maize cultivars is adapted to nutrient enriched topsoil reported by Zhang et al. [46].

$ZnSO_4$-coated urea where the nitrogen is slowly release into the soil and make available to the crop plant throught the cropping period which increases chlorophyll content and enhances the photosynthesis in plant. Application of Zn-coated urea also had the advantage of split application and banding of Zn close to the growing rice plants, which increased its uptake before applied Zn reacted with water and $CO_2$ in soil solution and converted it to $ZnCO_3$, which makes it less available to plants reported by Shivay et al. [39].

The residual effect of Zn at 5 kg per ha incubated with cow dung at 200 kg $ha^{-1}$ was recorded higher grain yield, straw yield and zinc uptake in wheat due to the beneficial residual Zn availability in the soil (0.60 to 1.24 mg $kg^{-1}$) after harvest of soybean. Combined effect of cow dung and Zn increases the yield and higher uptake of Zn. Cow dung contain both macro and micro nutrients in it upon decomposition these are release into the soil solution which easily taken up by plant which intern enhances the growth and yield of the crop plants reported by Kulhare et al. [15] and Prashantha et al. [33].

## Seed Treatment of zinc

Seed priming is a low-cost technique of soaking seeds in a solution containing Zn (or other micronutrient) for a specified time after which the seeds are redried and sown. Due to the small amounts of Zn needed for seed priming and the ease of the process, this is a practical way to increase the content of Zn in seeds to enhance seedling vigor, plant growth and yields. if compared with soil Zn applications reported by Rehman et al. [36]. Harris et al. [13] reported that priming maize seeds in a solution with 1 per cent Zn for 16 hr. increased the content of Zn from 15 to 560 mg $kg^{-1}$.

Increase in growth and yield parameter due to seed treatment with $ZnSO_4$ which stimulate ensured the proper hydration, which resulted in enhanced activity of α-amylase that hydrolyses the macro starch molecules into smaller and simple sugars. The availability of instant food to the germinating seeds gave a vigorous start and leads to the early root development and secondary roots by that more nutrient uptake is possible at an early stage. Also, more enzyme activity is may be the reason. The increased and faster field emergence increases the resistance against biotic and abiotic stress reported by Kunjammal et al. [16], Muharrem et al. [25], Nitin et al. [28] and Hajira et al. [12].

Sowjanya et al. [41] reported that seed treatment with green zinc oxide @ 1250 ppm recorded maximum seed germination, mean shoot length, mean root length and seedling dry weight in pigeonpea The increase in length of shoot and root due to seeds with more test weight shall have higher potential and seedling growth, thus in turn increase the metabolic activity through micronutrients and its translocation leading to early germination, cell division and elongation of cells leading to improving seedling length.

Seed treatment with Nano ZnO (1 g $kg^{-1}$ seeds) was recorded higher plant height and branches might be due to increased nitrogen uptake in nano ZnO treatment which intern increase auxin activity and production of carbohydrates leading to accelerate meristematic activity at the shoot apex which intern increased leaf area and Laef area index which resulted in higher leaf area duration results in more plant height and branches reported by Raj and Chandrashekara [34].

## Foliar application of zinc

Foliar sprays with Zn have been used as an agronomic practice to supplement soil Zn fertilizer applications during plant growth stages of high Zn demand, particularly when soil and climatic conditions may limit the availability of soil-applied Zn reported by Fernandez and

Brown [9]. Foliar Zn applications are considered more effective than soil Zn applications to alleviate Zn deficiency symptoms when they appear during the crop cycle.

Majid et al. [19] reported that foliar application of $ZnSO_4$. $7H_2O$ @ 2g per Ll of water during booting and milking stage in wheat increases the grain yield, biomass yield, number of spike and fertile spikelet due to the enzymatic activity improvement, microelements effectively enhanced photosynthesis rate and translocation of photo-assimilates to the grain. Zinc foliar spray increased grain yield by increasing tiller production; importantly, an application at booting was more effective than at other stages. Foliar applied Zn decreased Cd concentration in the roots, straw and grain reported by Rehman et al. [37].

The application of POP (RDF+ FYM+ Bio fertilizer) + foliar application of Zn as Zn $SO_4$ @ 0.5 per cent + B as solubor @ 0.2 per cent increases the growth and yield of chickpea due to Zinc which serves as energy source for synthesis of auxin and stimulates metabolic activities and enzymatic activities in plant. Boron is involved in cell wall development, cell distribution root and shoot elongation of plants and pollen tube germination which might have contributed to better growth reported by Santosh et al. [38], Vimal et al. [44] and Manjunath et al. [20].

**Zinc as nano fertilizer**

Nanotechnology comprises the use of material with at least one dimension smaller than 100 nm. The small size and hence high surface area to volume ratio of nanoparticles may result in different physicochemical properties compared to their bulk counterparts. It has been suggested that the implementation of nanotechnology in fertilizer research can enhance nutrient uptake and fertilizer efficiency and thus lead to economic and environmental benefits. Nano fertilizers could be designed to release nutrients in a con-trolled way synchronized with plant demand, or be designed to prevent the immobilization of nutrients in the soil, or could be directly taken up by the plant and thereby improve the nutrient uptake reported by De Souza et al. [7].

Zinc oxide nanoparticles are among the most widely used manufactured nanoparticles in industrial, commercial and medicinal products. In a few recent studies, it was suggested that ZnO nanoparticles may have potential as fertilizers of improved effectiveness for soil and foliage application. Prasad et al. [32] demonstrated that treatment of peanut seeds with ZnO nanoparticles (25 nm) resulted in greater seed germination, seedling vigor, stem and root growth, pod yield and chlorophyll content than treatment with chelated bulk $ZnSO_4$. In a field experiment, foliar application of ZnO nanoparticles significantly increase pod yield and shelling percent compared to foliar Zn applied as chelated bulk $ZnSO_4$, even when the nanoparticle treatment was applied at a 15 times lower dose than the $ZnSO_4$. Another study investigated the effects of bulk ZnO and ZnO nanoparticles on germination, growth and biochemical parameters of cabbage, cauliflower and tomato reported by Singh et al. [40], Uma et al. [43]. Poornima and Koti [31] reported that application of nano ZnO as foliar spray at 500 ppm recorded significantly higher ear head length, harvest index, test weight, grain yield and grain Zn content in sorghum. The enhanced germination and seedling growth in common chickpea exposed to ZnO nanoparticles (20–30 nm) was related to the high levels of indole acetic acid measured in the sprouts reported by Pandey et al. [30].

Rajesh et al. [35] reported that 75 per cent N + Foliar application of chemically synthesized nano N @ 4 ml $l^{-1}$ + Foliar application of chemically synthesized nano Zn @ 2 ml $l^{-1}$ recorded significantly higher plant height, fresh cob yield, green fodder yield and harvest index in maize due to adequate supply nitrogen and zinc which might have accelerated the activity of enzyme and auxin metabolism in the plant, which in turn enlarge the cell and cell elongation resulting in taller plants. The improvement in yield parameters with seed priming with nano ZnO @ 800 ppm and nano $Fe_2O_3$ @ 800 ppm 30 minutes followed by Foliar application of nano ZnO @ 800 ppm and nano $Fe_2O_3$ @ 800 ppm leads to increased leaf area and total dry matter partitioning and there by increases source to sink ratio and in turn increases the productive tillers (per hill), panicle length (cm) and thousand grain weight (g) may be due to enhancement in photosynthetic activity and these resulted in the translocation of photosynthates and amino acids from the leaves and culms to the grain reported by Naveenkumar et al. [27].

## Conclusion

Zinc fertilizers will continue to be used in agriculture to sustain crop yields to meet the demand for food in a growing population. Since Zn deficiency in humans has become a problem of major concern, current fertilizer research programs seek to improve not only yields but also grain Zn concentrations to address both food and nutritional security. and quality. It has been experimentally shown that under Zn-deficient conditions the application of Zn fertilizers to the soil is an effective strategy to increase crop yields, whereas foliar Zn application is highly effective when the goal is Zn biofortification. Timing of foliar sprays is a critical factor that determines the effectiveness of foliar-applied fertilizer in increasing grain Zn concentrations.

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