

Agronomic Effectiveness of Zinc Sources as Micronutrient Fertilizers: A Comprehensive Review'

Abstract

Zinc naturally occurs in the earth's crust as part of rocks and ore minerals. The average concentration of zinc in the lithosphere is 80 mg kg^{-1} . While zinc is relatively immobile in soil, it is moderately mobile in plants. As a **vital micronutrient for both humans and animals**, zinc plays an essential role in plants as a catalytic, structural and regulatory cofactor for many enzyme reactions. It is necessary for the metabolism of carbohydrates, protein synthesis, the biosynthesis of growth hormones (particularly indoleacetic acid) and the maintenance of cell membrane integrity. Zinc deficiency is a widespread problem affecting both plants and humans in many regions of the world. To address this issue and improve plant zinc nutrition and yields, both soil and foliar zinc fertilizers have been applied. 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: the inner core, outer core, mantle and crust. At the planet's center, the inner core is a solid sphere of iron and nickel, with a radius of about 759 miles (1,221 km) and temperatures reaching 9,800 degrees Fahrenheit (5,400 degrees Celsius). Surrounding the inner core is the outer core, a layer approximately 1,400 miles (2,300 km) thick, composed of iron and nickel fluids. Between the outer core and the crust lies the mantle, the thickest layer, which consists of a hot, viscous mixture of molten rock about 1,800 miles (2,900 km) thick, with a consistency similar to caramel. The outermost layer, Earth's crust, averages about 19 miles (30 km) deep on land. Beneath the ocean, the crust is thinner, extending 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 collected from the surface and 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 naturally occurs in the Earth's crust as part of rocks and ore minerals. The average concentration of zinc in the lithosphere is 80 mg kg^{-1} ” (Lindsay [17]). The concentration of zinc in soil-forming rocks varies significantly. Basaltic igneous rocks generally have a high concentration of zinc ($48\text{--}240 \text{ mg kg}^{-1}$), whereas silica-rich igneous rocks like granite and gneiss have much lower zinc content ($5\text{--}140 \text{ mg kg}^{-1}$). Among sedimentary rocks, black shales have the highest zinc content ($34\text{--}1500 \text{ mg kg}^{-1}$), followed by shales and clays ($18\text{--}180 \text{ mg kg}^{-1}$) and sandstone ($2\text{--}41 \text{ mg kg}^{-1}$) 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 2nd or 3rd 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 the most geographically widespread micronutrient deficiency, which is limiting crop production. In a global study conducted in 30 countries by the Food and Agriculture Organization of the United Nations (FAO) to assess the micronutrient status of soils, it was estimated that approximately 30 per cent of the world’s agricultural soils are zinc deficient. Countries with extensive zinc-deficient areas include China, India, Iran, Pakistan and Turkey, where it is estimated that between 50 and 70 per cent of cultivated land is affected by zinc deficiency” as reported by Alloway [1]. Zinc deficiency has also been 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, while in others, both old and new leaves are chlorotic.

Necrotic spots - Death of leaf tissue in areas of chlorosis.

Bronzing of leaves - Chlorotic areas may turn bronze-colored.

Rosetting of leaves - Zinc-deficient dicotyledons often have shortened internodes, causing leaves to cluster on the stem.

Stunting of plants Small plants may result from reduced growth or reduced internode elongation.

Dwarf leaves ('little leaf') - Small leaves that often exhibit 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. $\text{pH} < 7.7 = \text{Zn}^{2+}$, $\text{pH} > 7.7 = \text{Zn}(\text{OH})^+$ $\text{pH} > 9.1 = \text{Zn}(\text{OH})_2$.
- **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 for carbon uptake during photosynthesis. While zinc is important for

photosynthesis in phytoplankton, concentrations above 0.05 mg L^{-1} are often considered toxic and can impair this process. Zinc plays a crucial role in the structure and function of many enzymes, including alcohol dehydrogenases (ADHs) of the MDR type (medium-chain dehydrogenases/reductases). In these enzymes, active site zinc participates in catalytic events, while structural site zinc maintains structural stability. Superoxide dismutases (SODs) are universal enzymes found in 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 recognized for its role in the mitochondria, where it plays a crucial part in the life-supporting process of ATP synthesis.

Types of Zinc Fertilizers

A. Inorganic Compounds

- Include ZnO , ZnCO_3 , ZnSO_4 , $\text{Zn}(\text{NO}_3)_2$ and ZnCl_2
- ZnO : nearly insoluble in water but soluble in acids
- $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$: 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
- Na₂Zn-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 refers to the degree of crop response per unit of applied micronutrient. From the perspective of a fertilizer technologist, an effective fertilizer is one that provides maximum plant response at the lowest application cost. The agronomic effectiveness of zinc fertilizers is primarily associated with the water solubility of the zinc source, although other factors such as placement and source type can also influence the efficiency of zinc uptake 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 the edible portions of crop plants, either through fertilization (agronomic biofortification) or plant breeding (genetic biofortification)” given by White and Broadley [45]. Biofortification aims to provide essential micronutrients to populations lacking access to other interventions Saeid & Jastrzębska,[49]. Since staple foods are affordable and widely consumed, biofortification of these crops is a key focus. While biofortification is not as efficient as food supplementation, it can help narrow the gap in micronutrient intake and enhance daily intake of vitamins and minerals across the lifespan, potentially reducing malnutrition and improving overall human health 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 + ZnSO₄ (soil applied 30 kg ha⁻¹) + FeSO₄ (soil applied 30 kg ha⁻¹) + foliar application of ZnSO₄ (0.50 %) and FeSO₄ (0.10 %) due to the plants uptake zinc primarily in its oxidized form, Zn²⁺. They employ various mechanisms for zinc uptake, including chelation. In this process, plants release siderophores compounds that bind zinc and improve its solubility, often involving bacteria. Another mechanism involves plants releasing protons (H⁺) and reductants from their roots to lower pH levels in the root zone, thereby increasing 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 including photosynthesis, which contributes to increased plant height and other growth and yield parameters. Zinc activates enzymes involved in the synthesis of specific proteins and is crucial for chlorophyll formation, carbohydrate synthesis and the conversion of starches into sugars in plants. Additionally, zinc aids in enhancing plant tissue resilience to 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 increase in fresh cob and fodder yield is attributed to improved micronutrient availability (Zn and Fe) facilitated by the formation of stable organometallic complexes with organic matter during enrichment. This process ensures prolonged nutrient release in the soil, protecting them from fixation and enhancing availability to plant roots throughout the cropping period. Moreover, it promotes higher accumulation and efficient translocation of photosynthates from source to sink, resulting in overall higher crop productivity reported by Srivastav et al. [42], Anilkumar and Kubsad [2] and Fakeerappa and Hulihalli [8].

The increase in protein content attributed to zinc fortification is due to zinc's role in nitrogen metabolism and protein synthesis. Enzyme activities such as nitrite reductase, nitrate reductase and glutamine synthetase increase, leading to a decrease in free NO_3^- concentration and a significant increase in soluble protein concentration in the shoots following zinc 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, such as EDTA (Ethylenediamine Tetraacetic Acid) is not susceptible to fixation because the chelating compound binds to zinc in a claw-like fashion.

This prevents phosphates from binding with zinc, thereby enhancing the bioavailability of 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 zinc application increased the production and activity of indole-3-acetic acid, which promotes root growth. These observations were noted during the flowering stage, when the tips of brace roots may be rooting at depths of 25–30 cm. The root systems of modern maize cultivars are adapted to nutrient-enriched topsoil reported by Zhang et al. [46].

ZnSO₄-coated urea where the nitrogen is slowly release into the soil and make available to the crop plant through the cropping period which increases chlorophyll content and enhances the photosynthesis in plant. The application of Zn-coated urea also benefited from split application and banding of zinc close to the growing rice plants. This method increased zinc uptake before the applied zinc could react with water and CO₂ in the soil solution, converting it to less available forms like ZnCO₃ for plants reported by Shivay et al. [39].

The residual effect of zinc at 5 kg per ha combined with cow dung at 200 kg per ha resulted in higher grain yield, straw yield and zinc uptake in wheat. This was attributed to the beneficial residual availability of zinc in the soil (0.60 to 1.24 mg kg⁻¹) after the soybean harvest. 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 involves soaking seeds in a solution containing zinc (or other micronutrients) for a specified time, followed by drying and sowing the seeds. This low-cost technique requires small amounts of zinc and is straightforward to implement and making it a practical method to increase zinc content in seeds. Seed priming enhances seedling vigor, plant growth and yields more effectively than soil zinc 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.

The increase in growth and yield parameters due to seed treatment with ZnSO₄ ensures proper hydration, enhancing the activity of α -amylase. This enzyme hydrolyzes complex starch

molecules into simpler sugars, providing instant food availability to germinating seeds and promoting vigorous initial growth 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] and Rehaman et al., 2024 [47] reported that seed treatment with green zinc oxide at 1250 ppm resulted in maximum seed germination, mean shoot length, mean root length and seedling dry weight in pigeonpea. The increased shoot and root length in seeds with higher test weight indicates greater potential for seedling growth. This enhancement is attributed to micronutrients promoting metabolic activity and facilitating their translocation, which accelerates early germination, cell division and cell elongation, thereby improving seedling length.

Seed treatment with Nano ZnO (1 g kg⁻¹ seeds) was recorded higher plant height and branches. The increase in nitrogen uptake with nano ZnO treatment may enhance auxin activity and carbohydrate production, which accelerating meristematic activity at the shoot apex. This, in turn, increases leaf area and leaf area index, resulting in prolonged leaf area duration and contributing to greater plant height and branching reported by Raj and Chandrashekara [34].

Foliar application of zinc

Foliar sprays with zinc have been employed as an agronomic practice to complement soil zinc fertilizer applications during plant growth stages that require high zinc demand, especially when soil and climatic conditions might restrict the availability of zinc applied to the soil reported by Fernandez and Brown [9]. Foliar zinc applications are considered more effective than soil zinc applications for alleviating zinc deficiency symptoms when they manifest during the crop cycle.

Majid et al. [19] reported that foliar application of ZnSO₄ · 7H₂O @ 2g per L of water during booting and milking stage in wheat increases the grain yield, biomass yield, number of spike and fertile spikelet due to foliar spray of zinc improved enzymatic activity and effectively enhanced photosynthesis rates, facilitating the translocation of photo-assimilates to the grain. Zinc application *via* foliar spray increased grain yield by boosting tiller production, with application at the booting stage proving more effective than at other stages. Additionally, foliar zinc application reduced cadmium concentration in roots, straw and grain

reported by Rehman et al. [37].

The application of POP (RDF+ FYM+ Bio fertilizer) + foliar application of Zn as Zn SO₄ @ 0.5 per cent + B as solubor @ 0.2 per cent increases the growth and yield of chickpea due to zinc serves as an energy source for auxin synthesis and stimulates metabolic and enzymatic activities in plants. Boron plays a role in cell wall development, cell distribution, root and shoot elongation and pollen tube germination, contributing to improved growth reported by Santosh et al. [38], Vimal et al. [44] and Manjunath et al. [20].

Zinc as nano fertilizer

“Nanotechnology involves materials with at least one dimension smaller than 100 nm. The small size and high surface area to volume ratio of nanoparticles often result in distinct physicochemical properties compared to bulk materials. Implementing nanotechnology in fertilizer research is proposed to enhance nutrient uptake and fertilizer efficiency, potentially offering economic and environmental benefits. Nano fertilizers can be designed to release nutrients in a controlled manner aligned with plant demand, prevent nutrient immobilization in soil or facilitate direct uptake by plants to improve nutrient absorption” reported by De Souza et al. [7] and Singh et al. [48].

Zinc oxide nanoparticles are extensively utilized in various industrial, commercial and medicinal products. Recent studies suggest that ZnO nanoparticles could potentially serve as highly effective fertilizers for both soil and foliage applications, enhancing their effectiveness. Prasad et al. [32] demonstrated that “treating peanut seeds with 25 nm ZnO nanoparticles resulted in greater seed germination, seedling vigor, stem and root growth, pod yield and chlorophyll content compared to treatment with chelated bulk ZnSO₄. In field experiments, foliar application of ZnO nanoparticles significantly increased pod yield and shelling percentage compared to foliar application of chelated bulk ZnSO₄, even when the nanoparticle treatment was applied at a dose 15 times lower than ZnSO₄”. 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 improved germination and seedling growth in common chickpea exposed to 20–30 nm ZnO nanoparticles was attributed to the elevated levels of indole acetic acid detected 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 Fe₂O₃ @ 800 ppm 30 minutes followed by Foliar application of nano ZnO @ 800 ppm and nano Fe₂O₃ @ 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 enhanced photosynthetic activity, there was increased 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 crucial in agriculture to sustain crop yields and meet the food demands of a growing population. With zinc deficiency in humans posing a significant concern, current fertilizer research programs aim to enhance not only yields but also grain zinc concentrations to address both food and nutritional security. It has been demonstrated experimentally that applying zinc fertilizers to the soil under zinc-deficient conditions effectively increases crop yields, while foliar zinc application is highly effective for zinc biofortification purposes. The timing of foliar sprays is a critical factor determining the effectiveness of foliar-applied fertilizers in increasing grain zinc concentrations.

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