



## Mitigating Abiotic Stress and Enhancing Crop Yield Through Micronutrient-based Nano Fertilizer

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### ABSTRACT

Micronutrient deficiencies are a critical barrier to sustainable agriculture, significantly impacting crop yield and quality worldwide. Iron(Fe), copper(Cu), and zinc(Zn) deficiencies are particularly prevalent in plants grown in calcareous soils due to their high alkalinity, low organic matter content, and unfavourable texture, which limit nutrient bioavailability. Conventional fertilizers often exhibit poor nutrient efficiency due to leaching, fixation, and volatilization, necessitating advanced solutions such as micronutrient-based nano fertilizers (MNFs). These nanomaterials leverage unique physicochemical properties, including high surface-area-to-volume ratio, enhanced solubility, controlled nutrient release, and increased bioavailability, to optimize plant nutrient uptake and mitigate soil nutrient depletion. This review explores the role of ZnO, CuO, and Fe<sub>2</sub>O<sub>3</sub> nanoparticles in improving nutrient use efficiency (NUE), enhancing photosynthetic activity, and promoting stress tolerance under various abiotic conditions, including salinity, drought, and heavy metal toxicity. Furthermore, it examines the environmental fate of nano-fertilizers, potential ecotoxicological concerns, and regulatory challenges associated with their large-scale application. While MNFs hold promise for revolutionizing precision agriculture and soil fertility management, further research is required to develop standardized formulations, assess long-term soil-microbe interactions, and integrate nano-enabled fertilizers into sustainable agricultural systems.

**Keywords:** Nano fertilizers, ZnO, CuO, Fe<sub>2</sub>O<sub>3</sub>, Abiotic stress mitigation, Sustainable agriculture.

### INTRODUCTION

As global population growth surges, so does the demand for food grain production. However, several challenges complicate efforts to meet this demand sustainably, including mismanagement of agricultural land, excessive fertilizer usage, climate change, environmental degradation, over-reliance on non-renewable resources, and rapid urbanization.

These factors contribute intensely to food shortages and intense pressure on agricultural systems. In India, where the population has exceeded 1.4 billion, it now surpasses China's population.<sup>1</sup> The need for record-breaking food grain production has reached unprecedented levels. Recently, India produced 342.3 million tons of food grains, surpassing the previous record by 5.32 million tons. Among the top ten food grain-producing states, Haryana ranks



sixth with an output of 16.38 million tonnes over 4.47 million hectares<sup>2</sup>. However, this increased agricultural productivity also depletes essential soil nutrients, particularly micronutrients critical for crop development and human health. Although required in small amounts, micronutrients play pivotal roles in critical metabolic functions, including photosynthesis, nitrogen fixation, cation balance, and amino acid synthesis.<sup>3</sup> Deficiencies of micronutrients, especially zinc (Zn), iron (Fe), and copper (Cu), are widespread across South Asia, affecting countries like India, Pakistan, Afghanistan, Nepal, Bhutan, Sudan, and Bangladesh.<sup>4,5</sup> Approximately 36.5% of Indian soils are estimated to be deficient in zinc, with iron and copper deficiencies affecting 12% and 3.3% of soils, respectively. Specifically in Haryana, analyses show significant deficiencies in zinc (15.3%), copper (5.2%), and iron (21.6%)<sup>6,7</sup>. Such deficiencies underscore the need for targeted nutrient management strategies to ensure optimal crop productivity in nutrient-deficient regions. Among essential micronutrients, zinc, copper, and iron are critical for plant health and productivity.

Micronutrient deficiencies hinder crop growth and lead to physiological disorders, such as stunted growth, chlorosis, and leaf deformation, which reduce yields and quality<sup>8</sup>. To address nutrient deficiencies, farmers worldwide have traditionally used bulk fertilizers containing water-soluble salts, including sulfates or chelated forms such as  $\text{ZnSO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3$ , ammoniated zinc, and Fe/Zn chelates like EDTA and DTPA<sup>9</sup>. While effective, these fertilizers present challenges, including 40-70% nutrient leaching, runoff, nutrient fixation in soil, and reactivity, necessitating higher dosages<sup>10</sup>. Additionally, the overuse of fertilizers and pesticides for crop growth and nutrient density enhancement often results in soil degradation, water contamination, and environmental damage, further exacerbated by rising fertilizer costs.

In this context, nanotechnology has emerged as a promising approach to tackling agricultural challenges like nutrient deficiencies, land quality decline, and nutrient loss through leaching. Agriculture increasingly uses it to enhance the efficiency of inputs such as fertilizers. Nano-fertilizers, due to their high surface area-to-volume ratio, controlled release, targeted delivery, and reduced environmental impact, represent an innovative approach to enhancing nutrient absorption efficiency<sup>11,12</sup>. Nanoparticles like ZnO, CuO, and  $\text{Fe}_2\text{O}_3$  have improved root size,

chlorophyll content, protein production, and yield.<sup>11</sup> In recent research,<sup>13</sup> Demonstrated that spraying rice with zinc oxide nanoparticles can enhance yield and nutrient density under heat-stress conditions, showing a 22.1% yield increase compared to untreated plants. Controlled-release formulations and nanoscale coatings are gaining scientific interest, as evidenced by an upward trend in related publications, particularly since 2017<sup>14</sup>.

As the agricultural sector strives to enhance crop yields sustainably, it becomes crucial to compare conventional fertilizers and nano-fertilizers to understand their effectiveness, impact on soil quality, and potential to fulfill modern agricultural demands (Fig. 2). Conventional fertilizers must be applied substantially due to low nutrient utilization efficiency and their adverse effects on soil quality. In contrast, nano fertilizers release nutrients gradually, potentially enhancing nutrient use efficiency without causing harmful side effects<sup>15</sup>. Adding ZnO nanoparticles to other fertilizers in zinc-deficient soil led to a 91% increase in barley productivity and improved resource utilization efficiency compared to conventional  $\text{ZnSO}_4$ , which only resulted in a 31% productivity increase relative to the control<sup>16</sup>. Nano-composite fertilizers demonstrate beneficial impacts on rhizosphere bacteria by promoting the production of secondary compounds and enhancing the development of plants. Additionally, studies show that using controlled-release fertilizers increased wheat yield and residual soil mineral nitrogen by 6% and 10%, respectively, while reducing leaching and runoff losses by 25% and 22%, respectively, compared to bulk fertilizers<sup>17</sup>. Conventional fertilizers are costly and can harm human health and the environment. In contrast, nano fertilizers are crucial for sustaining soil productivity and improving crop production<sup>18</sup>. Nano fertilizers represent sophisticated farming resources created to deliver micronutrients to soils in a regulated way, and the advantage of nano fertilizers is their nanoscale size, enabling them to penetrate soil, water, and plants. Nano fertilizers are gradual-release agents that address soil acidity, moisture, and temperature fluctuations, promoting more effective plant growth<sup>19</sup> and present significant potential to enhance resource utilization efficiency, optimize costs, and minimize environmental degradation<sup>20</sup>. Therefore, this study investigates the efficacy of ZnO, CuO, and  $\text{Fe}_2\text{O}_3$ -based nano fertilizers in alleviating abiotic stress and enhancing crop yield, presenting a sustainable and efficient alternative to conventional bulk fertilizer applications.

### Deficiency of micronutrients

While macronutrients like nitrogen, phosphorus, and potassium are vital for plant growth, micronutrients such as copper, zinc, and iron play equally crucial roles in enhancing crop quality, boosting yields, and ensuring sustainable agricultural practices<sup>21</sup>.

A 2017 study by ICAR identified significant micronutrient deficiencies across India. The ICAR-All India Coordinated Research Project on Micro and Secondary Nutrients and Pollutant Elements in Soils and Plants (AICRP-MSPE) analyzed over 200,000 geo-referenced soil samples from various districts as shown in Table 1. Micronutrient deficiencies are increasingly prevalent in extensively cultivated crops, including vegetables, oilseeds, pulses, and grains. While the widespread and consistent application of zinc fertilizers has significantly reduced zinc deficiencies, multi-micronutrient deficiencies are emerging as a critical challenge in modern agricultural systems.<sup>22</sup> Nano-fertilizers are revolutionizing agricultural practices by enhancing the efficiency of micronutrient delivery. For example, zinc and copper oxide nanoparticles address soil deficiencies, promote root elongation, and plant growth.<sup>23</sup> And improve crop stress tolerance<sup>24</sup>. Iron nano-chelates offer a promising solution for chlorosis-prone soils, providing targeted and efficient nutrient delivery that minimizes environmental impacts.<sup>25</sup> Future strategies should integrate traditional soil fertility management practices with advanced nano-technologies to create a synergistic approach. Precision agriculture tools like drones and IoT-based sensors can further optimize the application of micronutrients, ensuring sustainable and productive farming systems.

### Release mechanisms of coated micronutrient-based nano fertilizers

Several delivery routes exist for micronutrient nano fertilizers, such as applying nanoscale fertilizers through foliar and soil applications and integrating nanoscale additives and composites to enter plant systems. In soil, MtNPs can be taken up by root hairs where carrier proteins are attached, and nano fertilizers can enter cells by endocytosis, ion channels, or aquaporin<sup>26</sup>. Several studies on the release of micronutrients from coated metal nanoparticles (MtNPs) suggest that a soil water concentration/pressure gradient plays a key role in nutrient release. The primary mechanism for nutrient release from polymer-coated fertilizers is the movement of nutrients from the fertilizer-polymer interface to the

polymer surface. Initially, water enters the ZnO-gum Acacia, CuO-chitosan, or chitosan-hydrogel  $Fe_2O_3$  nano-fertilizers as soil moisture. This causes the coating to swell, transforming the nano-fertilizer into a hydrogel<sup>27</sup>. As water is absorbed, the soluble components of the fertilizer dissolve and spread into the nanocomposite core. The gel releases these dissolved nutrients into the soil while the undissolved fraction breaks down due to moisture and microbial activity. Plants then absorb nutrients through root hair, leading to apoplastic or symplastic movements, reaching various parts of the plant<sup>27,28</sup>. Gum acacia/chitosan/hydrogel is essential for controlling the rate of nutrient release by preventing premature matrix breakdown and regulating water diffusion, ensuring that plants receive a steady supply of micronutrients over long periods. To optimize Nutrient utilization efficiency (NUE) and minimize ecological impact, controlled-release micronutrient fertilizers (CRNFs) provide a practical and promising solution by supplying plants with needed nutrients. These nano-fertilizers are engineered to deliver nutrients gradually at the targeted plant site, activated by moisture, pH, and temperature conditions. Integrating with carrier molecules enhances nutrient delivery to crops, minimizes environmental risks, and boosts crop yields. Nutrient release from coated nano fertilizers occurs in three phases from the fertilizer core: (1) the initial phase, (2) the steady release phase, and (3) the decline phase. During the initial phase, the difference in vapor pressure across the coating fuels allows water vapor to penetrate the granule, dissolving a small portion of the solid fertilizer. The difference in vapor pressure across the coating drives this reaction, with condensation occurring in the spaces between the core and its coating. The time it takes to fill the internal space of the granule with sufficient water is a crucial factor contributing to the lag period. After achieving an equilibrium state, the size of the granule remains almost constant. The efficiency of chitosan-coated nano urea as a slow-release fertilizer was investigated and compared with commercial urea. The coated nano urea significantly enhanced soil properties, improved plant growth, and reduced nitrate leaching. Nano-fertilizers play a significant role in sustainable agriculture. The present work proposes a new formulation of coated nano urea for the slow and sustainable release of nitrogen. Bare nano urea and a nano urea/chitosan nanocomposite were synthesized, and their structural, morphological, and thermal characteristics were studied using X-ray diffraction, Fourier-transform infrared spectroscopy, scanning electron microscopy,

and thermogravimetry. In addition, the protein content, free radical scavenging activity, and phenolic content were also found to be significantly higher in NUCNC-fertilized plants. The doses of the applied fertilizer have been observed to play an important role in plant growth. This study demonstrated that NUCNC could be potentially utilized as an alternative to commercial urea for sustainable agriculture<sup>27-29</sup>. When enough saturated solution accumulates within the granule, it triggers a continuous release of nutrients. The release rate remains steady as long as the saturated liquid within the granule is in equilibrium with the solid fertilizers. The consistent saturation level keeps the pushing force for fertilizer transport constant due to the reduced concentration in the adjacent liquid mixture. The level of the internal liquid mixture drops as the bulk fertilizer at the center dissolves during the third release phase, referred to as the decay phase. In the decline phase, nutrient discharge decreases as the granule's internal liquid level drops due to nutrient dissolution and water movement, reducing the driving force for release<sup>29</sup>. Nutrient release from controlled-release nitrogen fertilizers is mainly driven by four mechanisms: absorption, swelling, osmotic pressure, and diffusion<sup>30</sup>. Kumar *et al.*, described a starch-based polyvinyl alcohol (PVA) polymer designed for the controlled release of copper and zinc nanoparticles embedded in carbon nanofibers (CNF). In a pot experiment with chickpea (*Cicer arietinum*), when delivered via foliar application, this nanoscale additive fertilizer offered benefits such as better water absorption, increased water retention, improved water transport, cell wall extension, and soil stabilization<sup>31</sup>.

#### **Mode, translocation, and accumulation of nano fertilizers**

Nano fertilizers can be applied through various methods, including soil treatment, seed priming, foliar treatment, aeroponics, coating, emulsion, etc. Choosing the proper method for applying nano fertilizer is vital for vegetative development, as it varies according to nutrient availability, environmental factors, and soil characteristics. The uptake of nanoparticles depends on plant species, the size, chemical configuration, and concentration of the nanoparticles.<sup>32-35</sup> (Fig. 3) Proper application of nanoparticles can increase nutrient utilization efficiency, boost harvest output, minimize environmental harm, and promote sustainable agricultural practices. Soil nutrient deficiency can be managed effectively by using NPs for seed treatment and soil application instead of foliar application.<sup>36</sup>

#### **Foliar spray**

Foliar spray involves directly applying liquid fertilizers onto the leaves or foliage of plants. The absorption of nanoparticles can occur through stomata, hydathodes, cuticle penetration, and wounds, although it depends on particle size. Foliar fertilization provides rapid plant utilization and requires less time than soil application to address the observed deficiencies. The NF applied through this mechanism enters mainly via the stomatal pore and moves either apoplastically or symplastically to vascular bundles for translocation in the plant. Foliar spray presents several benefits over soil application, such as quicker responses, reduced leaching and runoff, enhanced nutrient absorption, and stimulated plant growth<sup>37</sup>. Studies have shown its effectiveness in boosting plant growth and yield. For instance, applying micronutrients like iron, zinc, and manganese via foliar spray has enhanced snap bean growth, increased yield, improved pod morphology, and enhanced nutritional quality<sup>38</sup>. Another study found that the foliar application of copper nanoparticles onto tomatoes led to an 80% enhancement in fruit yield while a 30% reduction in copper use compared to traditional copper-based fungicides<sup>39</sup>. However, the time of application is critical (morning or evening) as the opening of stomata during the foliar application is crucial for nutrient absorption. Overuse can damage plants, and multiple applications may be necessary, as they can be washed away by rain, or the plant must possess adequate leaf surface area for absorption.<sup>36</sup>

#### **Soil application**

Soil application, the prevalent method, involves mixing nano fertilizers with soil, facilitating interaction with plant roots for absorption onto the root surface and penetration into root cells via endocytosis, lenticels, and biotransformation. Nano fertilizers can be associated with soil particles and microorganisms, changing their interactions and effectiveness. Controlled-release or slow-release fertilizers ensure a consistent nutrient supply, promoting plant growth and yield. While this approach is dependable and can yield long-term effects of nanoparticles, it can be costly and poses regulatory hurdles<sup>40</sup>. Several studies have indicated that the gradual and sustainable release of nutrients like copper, zinc, and iron from fertilizers enhances nutrient use efficiency in tomato plants more effectively than commercial fertilizers, resulting in higher yields.<sup>11</sup>

### Seed priming

Seed priming, a pre-sowing technique, modifies the physiological characteristics of seeds, facilitating seed sprouting and improving vegetative growth and plant maturation through the regulation of signaling and metabolic pathways. This method entails soaking seeds in nano fertilizers, significantly improving the outcomes while reducing the fertilizer application by half<sup>41</sup>. Nano-biofertilizer penetrates seed pores, internally disperses, and activates plant hormones that stimulate growth, operating as a stimulant, increasing germination rate and seed development. A study by Nciizah *et al.*, demonstrated that using low concentrations (e.g., 0.01% B) and longer priming durations of Zn, B, and Mo significantly enhanced germination percentage, reduced seedling emergence time by 94% and increased seedling biomass and chlorophyll content by up to 58%, enhancing maize crop productivity.<sup>42</sup>

### Nano fertilizer applications in mitigating abiotic stresses: saline, drought, and heavy metal conditions

Crop yield is often constrained by the quality of irrigation water, which is typically evaluated based on parameters such as salinity, sodium adsorption ratio (SAR), and calcium, magnesium, and sodium levels.<sup>43</sup> Furthermore, the presence of heavy metals such as arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), iron (Fe), manganese (Mn), and zinc (Zn) has a substantial impact on water quality.<sup>44</sup> High concentrations of salts and heavy metals in irrigation water degrade water quality, leading to their accumulation in cultivated plants and agricultural soils.<sup>44</sup> The widespread use of wastewater, which often contains toxins, for irrigation has further exacerbated the problem. This practice introduces contaminants into the food chain, raising long-term health concerns for humans and animals.

### Saline conditions

Sol saline soil impacts approximately 950 million hectares of productive fields, with<sup>43</sup> million hectares of arable land experiencing anthropogenic soil salinization, resulting in a 50% decline in global agricultural output.<sup>45</sup> The concentration of salts in irrigation water directly influences crop growth and yield. However, its effect on soil permeability is more complex (Fig.4) higher salinity in irrigation water enhances soil permeability. In contrast, increased sodium (Na) concentration reduces soil permeability in response to sodic and saline conditions. (Anon,

n.d.). Excessively high sodium (Na) levels lead to soil sodicity, crust formation, increased runoff, erosion, and poor aeration. It also negatively affects the soil's hydraulic properties, including percolation rate and electrical conductivity. The potential risk of sodicity from irrigation water has traditionally been evaluated using the Sodium Adsorption Ratio (SAR) (Eq. 1), which relies on the cation configuration of the water.

$$SAR = \frac{C_{Na}}{\sqrt{\frac{C_{Na} + C_{Mg}}{2}}} \quad (1)$$

Here, C denotes the ionic concentration measured in millimoles of charge per litre, Na denotes sodium, calcium (Ca), or magnesium (Mg)<sup>43</sup>.

Salinity alters several physiological processes in plants, such as lowering photosynthetic efficiency, disrupting stomatal conductance, impairing gas exchange, and affecting plasma membrane integrity. Additionally, it causes the generation of toxic oxidative species such as Superoxide anion ( $O_2^-$ ), Hydrogen peroxide ( $H_2O_2$ ), singlet oxygen ( $^1O_2$ ), and hydroxyl radicals ( $OH^*$ ), Peroxyl radicals ( $ROO\bullet$ )<sup>47</sup> Various materials, such as hydrogel, biochar, magnetic bentonite, and nanomaterials or nanoparticles, have been studied to mitigate these effects and improve poor water quality.<sup>48</sup> Nanomaterials have been utilized to eliminate pollutants from polluted water. Applying copper nanoparticles (CuNPs) improved plant growth under salt stress by boosting growth parameters, gas exchange metrics, and photosynthetic compounds. In addition, the accumulation of osmolytes, hydrogen peroxide ( $H_2O_2$ ), malondialdehyde (MDA), total phenols, and flavonoids was decreased by CuNPs, which lessened oxidative damage. At the same time, they increased the activity of antioxidant enzymes.<sup>48</sup> Amira *et al.*, 2015 applied Zinc and iron nanoparticles through a foliar spray with a standard Hoagland solution. There was a decrease in sodium and chloride ion levels and an enhancement in nitrogen, phosphorus, potassium, magnesium, manganese, iron, and zinc.<sup>45</sup> Total chlorophyll, carotenoids, proline, carbohydrates, crude protein levels, and non-enzymatic and enzymatic antioxidants were also elevated. Various studies show that ZnO nanoparticles increase the antioxidant enzyme activity (superoxide dismutase (SOD), ascorbate peroxidase (APX), and glutathione reductase (GR) system), and nutrient absorption.<sup>49</sup>

### Drought stress conditions

Drought is one of the most significant

abiotic stresses that negatively affect crop plants, causing a reduction in seed development, lower yields, and decreased nutritional quality<sup>50</sup>. More than 40% of the global population faces drought stress annually, and by 2030, 7 billion people may be forced to migrate from arid regions. Due to drought-induced stress, plants experience oxidative stress and other physiological and biochemical reactions. Plants employ various mechanisms to cope with drought, including producing oxidative species, synthesizing stress hormones such as abscisic acid and ethylene, changes in root and shoot structure, stomatal closure, and reduced chlorophyll production<sup>51,52</sup>. These responses lead to both short-term and long-term reactions. When the stress is short-lived, the plant's responses are likewise temporary, including decreased carbon fixation, stomatal reduction, disrupted osmotic balance, growth, and water movement alterations, and the transmission of signals indicating cell dehydration. These short-term responses typically do not cause lasting damage if normal conditions are restored quickly. However, during prolonged drought stress, irreversible changes occur in the plant, ultimately leading to death<sup>53</sup>. The primary ROS include superoxide anion radicals, hydroxyl radicals, hydrogen peroxide, and singlet oxygen. These molecules can harm cellular membranes, disrupt photosynthesis, and impair electron transfer in chloroplasts and mitochondria<sup>50</sup>. The resulting disturbances under such unfavorable conditions cause a decline in crop yields. Plants use their antioxidant defense systems to scavenge the damaging reactive oxygen species (ROS) in response to these stressors<sup>54</sup>. The severity of the water deficit, the plant's developmental stage, and its genotype affect how strongly the plant defends itself<sup>55</sup>. Antioxidant enzymes such as ascorbate peroxidase (APX), catalase (CAT), and peroxidase (POX) are part of the plant's defense mechanism. Additionally, it contains suitable solutes such as proline and glycine betaine, as well as antioxidants like glutathione,  $\alpha$ -tocopherols, and phenols<sup>56</sup>. Samota *et al.*, 2024 demonstrated that seed priming with iron (Fe), zinc (Zn), and methyl jasmonate (MeJA) under drought stress significantly enhanced several biochemical and physiological responses in plants: carotenoids (10–19%), abscisic acid (18–50%), proline (60–80%), superoxide dismutase activities (27–62%), ascorbate peroxidase (46–61%), catalase (50–80%), and NADPH oxidase (16–30%). When copper (Cu) and zinc (Zn) nanoparticles (NPs) are applied to wheat plants, oxidative stress defense enzyme activity is increased. The water retention

capacity lowers the levels of thiobarbituric acid, influences the precipitation of reagents, stabilizes the levels of light-absorbing pigment in the leaves, and lessens the effects of stress<sup>57</sup>. Furthermore, under dry conditions, Cu NPs applied to maize have been demonstrated to raise anthocyanin, chlorophyll, carotenoid, plant biomass, and leaf water content<sup>58</sup>. The study by Ghani *et al.*, increased the antioxidant defense system, nutrient absorption, and osmolyte accumulation in cucumber seedlings<sup>59</sup>. Reduction in ROS lipid peroxidation is observed in ZnO NP-treated seedlings. In addition, the foliar spray of Zn and Fe nanoparticles increases antioxidant enzyme activity, proline and sugar content, and leaf size, and improves Pinto beans' seed quality<sup>60</sup>. Under drought stress conditions, applying foliar nano iron oxide enhances soybean seed production by 40.12 and 32.60% in water deficit conditions, increasing the oil content of seeds by 61%.

#### Heavy metal stress

Heavy metal (HM) strain impacts plants' physiological and biochemical properties. Several approaches are employed to mitigate this stress in plants. These include:

- (1) Minimizing the concentration of bioavailable heavy metals in the topsoil.<sup>62</sup>
- (2) Regulating the functioning of genes related to the transport of heavy metals in plants.<sup>63</sup>
- (3) Strengthening the plant's Oxidative stress defense system and optimizing physiological processes.<sup>64</sup>
- (4) Stimulating the synthesis of protective compounds like organic acids, metal-binding peptides, and rhizome secretion.<sup>63,65</sup>

Nanoparticles (NPs) in the soil can absorb and transform heavy metals (HMs), reducing their movement and bioavailability. For instance,  $\text{Fe}_3\text{O}_4$  nanoparticles have been shown to reduce the transferability of cadmium and other HMs in the soil. Additionally, specific nanoparticles can enhance soil properties; for instance, hydroxyapatite nanoparticles can discharge phosphate and raise soil hydrogen ion concentration, thereby mitigating the detrimental impacts of heavy metals in the soil<sup>66</sup>. The plant is protected by the apoplastic transport barriers in the rhizosphere, which regulate the flow of oxygen, cations, anions, and water<sup>63</sup>. Heavy metal (HM) aggregation in the underground root may be restricted by the influence of nanoparticles (NPs) on the development of these barriers<sup>67</sup>. However, as plant roots also have a variety of ion and protein

channels within the cell wall that can simultaneously transport heavy metals, more than apoplastic polymeric barriers may be required to reduce HM stress. Additionally, specific NPs can transport and regulate metal in plants, strengthening the cell wall barriers to block HM entry. Most NPs build up in cell walls, forming compounds with metals to render them inert. These complexes stick to the cell's surface<sup>64</sup>, inhibiting the movement of heavy metals (HMs) within the plant and diminishing their biochemical function. Furthermore, natural acids that build up in root structure and foliage cell walls can chelate heavy metals, alleviating the detrimental impacts of stress. MNPs have also been shown to boost the production of protective structural agents. An alternative strategy for alleviating heavy metal (HM) stress involves stimulating the Plant antioxidant defense system<sup>68</sup>. Plants naturally produce Oxidative species through specific metabolic processes. For instance, ROS are continuously generated in chloroplasts and other cellular regions during respiration and photosynthesis. At low concentrations, ROS function as signaling molecules that contribute to growth, development, and defense<sup>68</sup>. However, excessive accumulation of reactive oxygen species (ROS) can adversely affect cell walls, cytoplasm, mitochondria, chloroplast proteins, and other cellular structures under stress conditions. Plants utilize essential free radical-scavenging enzymes, including superoxide dismutase (SOD), peroxidase (POD), glutathione reductase (GR), ascorbate peroxidase (APX), catalase (CAT), and monodehydroascorbate reductase (MDHAR), to counteract ROS. Furthermore, ROS are scavenged by low-molecular-weight, non-catalytic substances such as ascorbic acid and tocopherol and carotenoids, polyphenols, and flavonoids<sup>69,70</sup>. Stress triggers the creation of shikimate-phenylpropanoid and the metabolism of galactose, alanine, aspartic acid, and ascorbate, among other metabolic pathways involved in ROS detoxification, which contribute to reducing oxidative stress in plants. In their 2019 study, Rizwan *et al.*, investigated how foliar application of ZnO nanoparticles (NPs) affected *Zea mays*'s cadmium (Cd) absorption and antioxidant enzyme activity. Their results demonstrated that ZnO NPs applied at 50, 75, and 100 mg/L concentrations significantly reduced Cd uptake in roots by 18%, 33%, and 53%, and in maize shoots by about 12%, 23%, and 61%, respectively. Additionally, ZnO NPs enhanced biomass in the roots and shoots of maize seedlings and elevated antioxidant enzyme activity<sup>71</sup>.

### Current and future outlook of nano fertilizer

After the 1960s, food grain production increased due to synthetic fertilizers and pesticides, severely affecting the environment. We must ensure that nano fertilizer decreases environmental damage rather than increases it.<sup>72</sup> Nano fertilizer holds the potential to enhance nutrient delivery to plants, thereby increasing yield production while mitigating the environmental drawbacks associated with chemical fertilizers. Diverse studies have investigated nanomaterials like nano chitosan and metal oxide nanoparticles, revealing improved soil nutrient absorption rate and retention capacity. Considerable advancements have been made in developing controlled-release fertilizers, which release nutrients gradually, thus reducing the need for frequent application.

Future studies on nano fertilizers should prioritize creating cost-effective and environmentally friendly methods for synthesizing nanomaterials, optimizing their physical and chemical properties, and decreasing the risk associated with their use. We need eco-friendly innovations and artificial intelligence technologies to create durable, decomposable, and future-oriented sustainable products. These technologies would significantly enhance natural resource applications and lessen environmental impact.<sup>73</sup> Nano sensors in Nano fertilizer could allow real-time monitoring, inform the right time to apply NFs, and decrease nutrient waste.<sup>74,75</sup> Precision agriculture incorporates drones equipped with multispectral cameras to capture images that detect nutrient levels in the soil. This technology enables farmers to optimize resource usage by avoiding over-applying nutrients to their crops.<sup>74,76</sup>

Furthermore, it is imperative for research efforts to comprehend the environmental and human health implications of nano fertilizers. Simultaneously, there is a need to establish a regulatory framework and standardized protocols to enhance their safety and appropriate utilization.<sup>77</sup> Research is progressing to form Nanocomposites to provide nutrients through intelligent delivery systems, which could aid in balancing the crop's nutrient supply.<sup>23</sup> Research is required on how nutrients are delivered in the plant system and the effects and eventual destiny of nano fertilizer in the environment.<sup>78</sup>

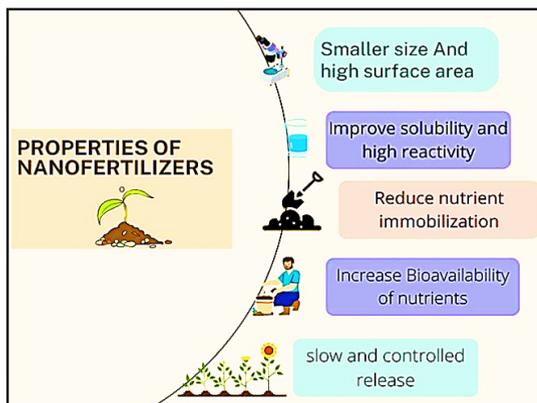


Fig. 1. Advantageous properties of nanoparticles applicable as Nano fertilizers

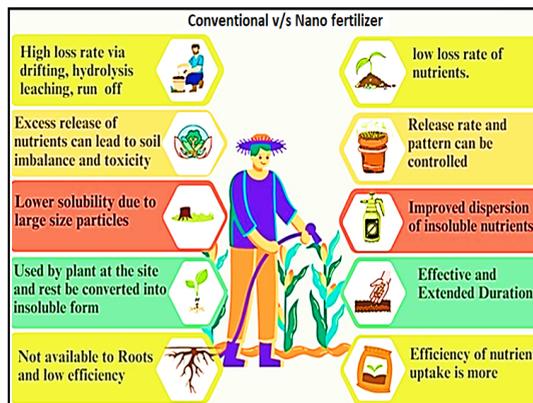


Fig. 2. Comparison between Conventional Fertilizers and nano fertilizers

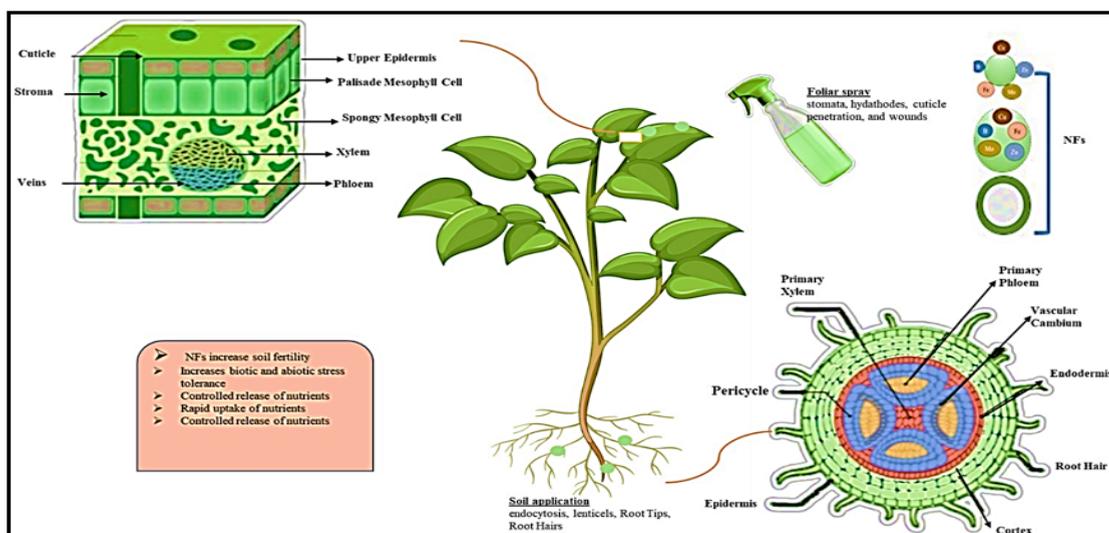


Fig. 3. Illustration of application uptake and movement of applied Nano fertilizers (NFs)

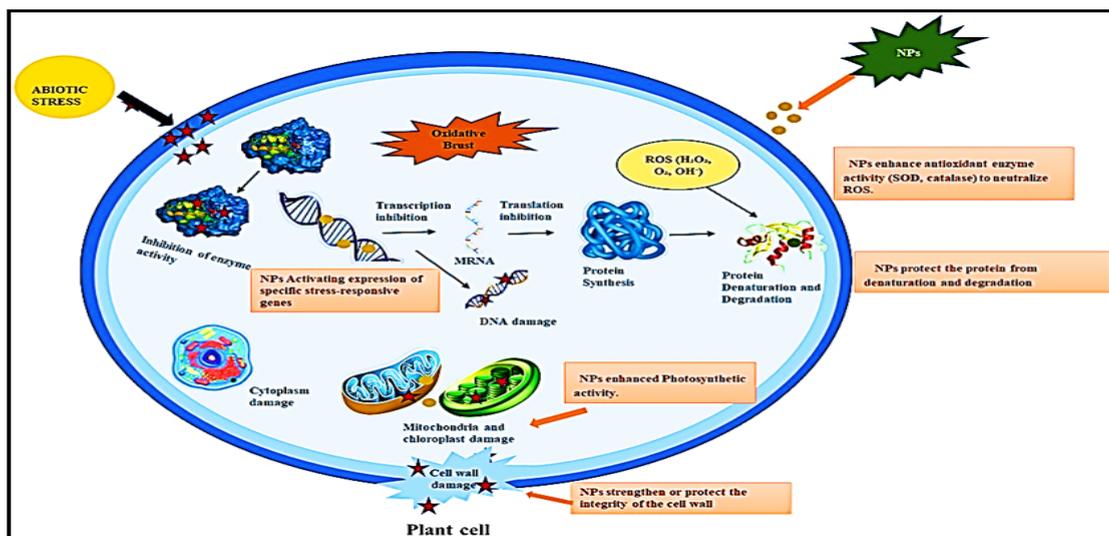


Fig. 4. Effects of abiotic stress on cellular components and the protective functions of Nanoparticles (NPs)

**Table 1: Micronutrient deficiencies in Indian soils**

Micronutrient	Overall Deficiency (%)	Regions with Severe Deficiency (>50%)	Regions with Moderate Deficiency (30-50%)	Regions with Low Deficiency (<20%)	Contributing Factors
Zinc (Zn)	36.5%	Rajasthan, Gujarat, Haryana, Punjab	Maharashtra, Telangana, Andhra Pradesh	Eastern states	Coarse-textured soils, high pH (>8.5), calcareous and sodic soils, low organic carbon
Iron (Fe)	12.8%	Karnataka, Tamil Nadu, Maharashtra, Gujarat, Rajasthan	Haryana, Punjab	Eastern and northeastern regions	Alkaline soils (pH >7.5), calcareous, aerobic soils, high redox potential
Copper (Cu)	4.2%	Southernmost regions of India	Southern and Western states Haryana, Punjab	Tamil Nadu, Uttar Pradesh,	Intensive farming practices, alkaline, calcareous soil, low organic carbon
Boron (B)	Varies regionally Odisha, Jharkhand	Bihar, Gujarat, West Bengal,	Madhya Pradesh, Maharashtra	Northwestern and some central areas	Highly calcareous and acidic soils, leaching in sandy loam soils

**Table 2: Role of key micronutrients in plants and the potential improvements achieved by using nano-fertilizers (NFs).**

Micronutrient	Role of elements	Improvement in plant growth by NFs	Physiological Toxicity	Reference
Zinc	Activates enzymes (Carbonic dehydrogenase, Phosphorylase, Carboxylase) Helps in tryptophan synthesis and precursor for auxin production	Reduced reactive oxygen species and chlorophyll fluorescence activity Improved photosynthetic rate, high chlorophyll and carotenoid content Increased level of protein and carbohydrates.	Excess Zn enhances Fe deficiency.	15,40,79-83
Copper	Associated with enzymes. Example-Lactase, oxidase  Synthesis of lignin Required for synthesis of vitamin C (Ascorbic acid), which controls cell division, elongation, and differentiation.	Increase antioxidant enzymes like oxidase, catalase, peroxidase and Superoxide Dimutase), and decrease malondialdehyde content. Mitigate oxidative stress Promote stomata closure, which reduces water evaporation	Growth inhibition photosynthesis inferences  Increase oxidative stress, chlorosis	22,58,81,84
Iron	Constituents of enzymes like peroxidase and catalase (Present in peroxisomes) help in the formation and dissociation of peroxidase Constituent of ferredoxin and cytochrome (a protein essential for electron transfer) Help in chlorophyll synthesis, energy production, Nitrogen reduction, and biological N <sub>2</sub> fixation.	Increase in the level of photosynthesis  Increase physiological parameters, including root growth and antioxidant enzymes such as catalase, peroxidase, and SOD, polyphenyl oxidase.	Bronzing, Stunted root system,  Deficiency of other micronutrients	85-89
Manganese	Helps in the production of chlorophyll during photosynthesis (transferring electrons through chlorophyll to convert CO <sub>2</sub> into carbohydrates and release O <sub>2</sub> from H <sub>2</sub> O) Promotes faster seed germination and hastens the maturation process. Increase availability of P and Ca	Increased synthesis of flavonoids, amino acids, and lignin  Increase in the efficiency of herbicides and pesticides	Causing oxidative stress, chlorosis in leaves (interveinal and marginal) Necrotic leaf spot	90-92

**Table 3: Shows the comparative effects of nanoparticle-based fertilizers on plant growth, stress tolerance, and yield across different plant species and environmental conditions.**

Fertilizer composition	Method Used	Particle size	Plant culture	Stress	Experimental conditions	Experimental Result	References
Fe, Zn, and Mg	Green Synthesis	ZnO-9.5nm, Fe <sub>3</sub> O <sub>4</sub> -7.8nm and MnO-10.5nm	Cabbage and lupin plants	----	Foliar Spray	Lupin Plants- 6% height increase, 19% root size increase, 3.5% increase in chlorophyll content, 300% increase in leaf area.	93
Zn	Chemical method	ZnO (50nm)	Cucumber	Drought	Foliar Spray	The antioxidant defense system is increased, and nutrient absorption and osmolytes accumulate.	24
Zn	Chemical method	ZnO (30nm)	Cotton	Drought	Foliar spray	Increase plant growth and yield, and increase antioxidant enzyme activity	94
Fe	Chemical method	Fe <sub>3</sub> O <sub>4</sub> (50–100nm)	Soyabean	Drought	foliar Spray	40.12% and 32.60% increase seed yield under drought stress conditions,	61
Zn and Fe	Green Synthesis	Less than 100nm	Pinto bean	Drought	foliar Spray	Increase antioxidant activity, proline content, soluble sugar, and leaf area	60
Cu and Se	Chemical Reduction Meth	SeNPs and CuNPs (5–18 and 35–42 nm), respectively,	Strawberry	Drought	Foliar Spray	Improving the growth, quality, and physiological characteristics	95
Zn and Fe	Chemical method	ZnO and Fe <sub>3</sub> O <sub>4</sub> (30nm and ranging from 10 to 30nm)	Wheat (Triticum aestivum)	Drought	Foliar Spray	NPs increased the proline, soluble sugars, and enzyme activities, and 88% increased grain yield.	96
Zn and Fe	Chemical method	Less than 100nm	Dragonhead (Dracocephalum moldavica)	Drought	Foliar Spray	Enhanced level of total chlorophyll content, above-ground plant biomass, flavonoid, and anthocyanin	97
Cu and Se	Green Synthesis	100–300 nm for Se and 350–500 nm for CuO	Tomato	Salinity	Foliar Spray	Increased tomato output (2.07 kg/plant), 9.24% increase in soluble solids content	98
Cu	Green Synthesis	9-18nm	Barley	Salinity	Seed Priming	Improved plant growth under salt stress, photosynthetic pigments, and gas exchange parameters	48
Polyvinylpyrrolidone-coated Cu Nps	Chemical Reduction Method	420 nm	Wheat	Salinity	Foliar Spray	Reduced oxidative Stress	99
Zn and Cu	Green Synthesis	Less than 100nm	Basil plant	Salinity	Foliar Spray	Significant effect on chlorophyll content,	100
Zn and Fe	Chemical Precipitation	ZnO (10-15 nm) and Fe <sub>3</sub> O <sub>4</sub> (10 to 12 nm)	Moringa peregrine	Salinity	Foliar Spray	Decrease in sodium and chloride levels and increase the N, P, K, Mg <sup>2+</sup> , Mn <sup>2+</sup> , Fe,	45

Zn	Chemical Method	68.1 nm	Rice	Heavy Metal (As, Cd, And Micronutrients)	Foliar Spray	and Zn concentrations and carotenoid levels.	101
S and Cu	Chemical Method	37-61nm	oilseed rape	Heavy Metal (Cu)	Seed Priming	Highest excretion of root exudates and the most significant arsenic (As) uptake reduction.	102
Fe	Chemical co-precipitation Method	Fe <sub>3</sub> O <sub>4</sub>	Coriander	Cd and Pb toxicity	Seed Priming	Increased shoot and root length and dry weight by up to 28.2%.	103
Zn	Green synthesis	(450 ppm and 600 ppm)	Maize (Zea mays)	Heavy Metal (Cd)	Foliar Spray	Increase antibacterial activity	9
Zn	Chemical Synthesis	Less than 100nm	Rice and Serendipity Indica	Heavy Meta (Cd)	Seed Priming	Reduction in plant height (35.24%), biomass (43.86%), and yield (37.62%) due to cadmium exposure	104
Fe, Zn, and Cu	Chemical Synthesis	Less than 100nm	Wheat (Fayyad cultivar)	heavy metals	Foliar Spray	Increase Antioxidant activities, specifically peroxidase (61.5 and 122.5% in Y1801 and Hz43 roots, respectively)	105

## CONCLUSION

Nanotechnology is transforming modern agriculture by addressing critical challenges such as nutrient deficiencies, soil degradation, and environmental sustainability. Micronutrient-based nano fertilizers, mainly those containing zinc, copper, and iron, exhibit superior efficacy in enhancing crop productivity, nutrient uptake, and stress resilience compared to conventional fertilizers. Their controlled-release mechanisms significantly reduce nutrient losses, enhance soil health, and mitigate the environmental impact of excessive fertilizer. Nano fertilizers also play a pivotal role in alleviating abiotic stress conditions, including drought, salinity, and heavy metal toxicity. These fertilizers enhance plant performance under adverse environmental conditions by optimizing nutrient absorption and improving physiological tolerance mechanisms. Their ability to modulate antioxidant activity, regulate osmolyte accumulation, and enhance enzymatic functions underscores their significance in stress management and sustainable agriculture. Despite the promising potential of nano fertilizers, further research is required to comprehensively assess their long-term environmental impacts, regulatory implications, and economic feasibility. The integration of precision agriculture methodologies, including nano sensors and AI-driven monitoring systems, will improve the efficiency of nano fertilizer applications and maximize their agronomic benefits. Future investigations should focus on developing safe and sustainable nano-fertilizer formulations to facilitate their role in advancing resilient and productive agricultural systems. By leveraging nanotechnology, it is possible to establish sustainable farming practices that address the increasing global food demand while minimizing ecological consequences.

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## Author Contribution

**Manisha Lohchab**-Major contribution

in writing the manuscript, collection of data, and reviewing the research paper Vaishali Arora-She contributed significantly to editing the manuscript.

**Dr. Babita Khosla**-She supervised manuscript development with insightful contributions

and made the final edit to improve the quality of the manuscript.

#### Conflict of Interest

There is no competing interest in the manuscript.

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