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Nanoforms of Essential Metals: Agricultural Potential and their Impact on Soil Health

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Abstract: With the current scenario of population explosion, it is observed that imbalance has been created between food and nutrition supply and its demand. On 15th November, 2022 world population crossed the mark of 8 billion and is estimated to cross 11 billion by 2100 (UN, 2023). To solve the problem of feeding this ever-growing population and to cope with global climate change, nanotechnology can be a solution. Compared to other fields of nanotechnology application, like medicine, materials and energy, agriculture is still at infancy and hence have a scope of revolutionizing in this sector. Major classes of manufactured nanomaterials include, inorganic nonmetallic, metals and their alloys, and carbon based. Among these classes, essential metals *viz*. manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn) and molybdenum (Mo) are considered vital for growth of plants and thus have role in agricultural potential. Nanometals have various roles in enhancing agricultural potential, such as growth and yield promotion, induction of phytochemical production and providing tolerance against biotic and abiotic stresses. Although there are numerous benefits of nanometal application in the field of agriculture, these materials have negative impacts as well. These nanometals have the potency to alter the physical, chemical and biological health of soil. Hence, extensive research to be carried out before the full-fledged application of nanoforms of essential metals to determine optimum doses and application methods and utilize this potent entity for global welfare in a sustainable way.

Keywords: Nanoparticles, essential metals, biotic stresses, abiotic stresses, agricultural potential, soil health.

INTRODUCTION

Essential elements are vital for the growth and reproduction of plants, and they cannot be substituted by other elements. These elements play direct roles in plant metabolism, contributing to the formation of structural and functional components within plant cells. Insufficient availability of essential elements can result in harm and impair plant health. Several metals, including copper (Cu), iron (Fe), molybdenum (Mo), manganese (Mn), zinc (Zn), and nickel (Ni), fulfill these criteria as essential trace elements within plant structures (Barker & Pilbeam, 2015). Terrestrial plants possess specialized transport mechanisms that facilitate efficient absorption of essential metal ions from the surrounding environment. These mechanisms ensure proper distribution of these ions within different organs and tissues of the plant, as well as their sequestration within specific cellular compartments (Andresen *et al.*, 2018). Within plant cells, essential metals can exist in various biologically active forms, including hydrated ions, as cofactors within proteins, bound to nucleic acids, and associated with molecules such as amino acids, glutathione, nicotinamine, citrate, and malate (Juárez-Maldonado *et al.*, 2018). One of the notable chemical properties

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that holds great significance in determining the specific biological functions of essential metals is their redox activity. Copper (Cu) and iron (Fe), owing to their ability to exist in different oxidation states, play a catalytic role in facilitating redox reactions within enzyme active sites. This involvement in electron transport and cellular redox control underscores their importance in various biological processes.

Cu plays a distinct role in photosynthetic electron transport as the cofactor of plastocyanin (Droppa and Horváth, 1990). Additionally, Cu acts as a cofactor in the mitochondrial electron transport chain, alongside Fe (in the form of haem), supporting the function of cytochrome oxidase. Cu is also involved in the detoxification of reactive oxygen species (ROS), activating Cu/Zn superoxide dismutase (SOD) isoenzymes and ascorbate oxidase (Alscher *et al*., 2002; De Tullio *et al*., 2013). Furthermore, Cu-dependent oxidases such as laccase, polyphenol oxidase, and amine oxidase play crucial roles in wound healing and plant defense against pathogens (Li *et al*., 2019). Notably, Cu is present in the active site of ethylene receptors, thereby contributing to the perception of the hormone ethylene within plant cells (Li *et al*., 2019; Schott-Verdugo *et al*., 2019). SOD, an antioxidant enzyme, exhibits an isoform that operates in the presence of Fe. The roles of Cu/ZnSODs and FeSODs differ, with FeSODs specifically regulating the levels of reactive oxygen species (ROS) as signaling molecules (Alscher *et al*., 2002). Another protein involved in respiration, the alternative oxidase, binds to haem-Fe. Moreover, within the P450 superfamily, there exist multi-haem proteins that facilitate redox reactions and convert various secondary metabolites, including amines, fatty acids, and steroids. The P450 enzymes also play critical roles in multiple steps of lignin biosynthesis. In photosynthesis, Fe directly participates in the light reactions, being a component of cytochrome b_{559} in the photosystem II (PSII) reaction center and forming Fe_4S_4 clusters in photosystem I (PSI) reaction centers. The cytochrome b_6f complex, involved in electron transport, contains both haem and Fe-S clusters. Within the respiratory electron transport chain, Fe-S clusters are present in complex I and II, as well as in the cytochrome bc_1 complex. The availability of Fe is also essential for nitrate and sulfate metabolisms, as enzymes such as nitrate reductase (NR), nitrite reductase (NiR), and sulfite oxidase (SO) rely on haem-Fe (Vigani & Murgia, 2018). The enzymes NR and SO not only contain Mo in the form of molybdopterin, an organic cofactor, but this Mo is crucial for substrate binding and reduction. There are also other enzymes, such as aldehyde oxidases involved in abscisic acid and indoleacetic acid biosynthesis, as well as xanthine oxidase, that require Mo for their function. Interestingly, these Mo-dependent enzymes also possess a Fe_2S_2 cluster (Mendel & Hänsch, 2002).

Manganese (Mn) plays a critical role in plants as it serves as a central component of the water-splitting complex within the photosystem II (PSII) reaction center. Additionally, MnSODs, which are involved in detoxifying reactive oxygen species (ROS), are present in mitochondria and peroxisomes. Germin and germin-like proteins, located in cell walls, bind Mn and facilitate the production of hydrogen peroxide (H_2O_2) from oxalate. H_2O_2 acts as a signal for pathogen defense, an antimicrobial agent, and an inducer of lignification. Although there are enzymes (e.g., decarboxylases and dehydrogenases in the tricarboxylic acid cycle and phenylalanine ammonia lyase in the shikimic acid pathway of secondary metabolite synthesis) that do not directly bind Mn, they are activated in its presence (Schmidt & Husted, 2019).

Zinc (Zn) exhibits distinct biological functions and roles compared to copper (Cu) and iron (Fe) since it is not a redox-active metal. Unlike Cu and Fe, Zn does not catalyze redox reactions. Instead, it acts as a Lewis base at enzyme active sites or serves as a structural component of proteins. Zn is present as a cofactor in all six enzyme classes. Carbonic anhydrase, a crucial Zn-dependent plant enzyme, facilitates the interconversion of carbon dioxide and bicarbonate. Similar to Cu, Fe, and Mn, Zn is also involved in detoxification of reactive oxygen species (ROS) by binding to the active site of Cu/ZnSOD (Castillo-Gonzales *et al*., 2018). Several phosphatase enzymes contain Zn, with alkaline phosphatases featuring one magnesium ion (Mg^{2+}) and two Zn^{2+} ions at their active sites.

Purple acid phosphatases, on the other hand, possess an active site where one Fe^{3+} ion and one Zn^{2+} ion are bound. Regulatory role of Zn in phosphatases contributes to phosphate nutrition (Olczak *et al*., 2003). Another notable enzyme is S-nitrosoglutathione reductase, which governs nitric oxide metabolism and signaling, and relies on catalytic and structural Zn ions (Lindermayr, 2018). Zn also plays a role in gene expression regulation through the interaction of zinc-finger transcription factors with Zn, resulting in conformational changes that alter DNA-binding activity. Thus, Zn controls gene expression by regulating non-protein transcription factors (Takatsuji, 1998; Kumar et al., 2015). Ni is an exceptionally unique metal due to its exclusive role in the functioning of a single known plant enzyme called urease. Urease plays a vital role in detoxifying urea, which is the final product of protein and ureide breakdown. By catalyzing the recycling of nitrogen (N), urease contributes to this essential process (Fabiano *et al*., 2015).

In total, plant cells possess a minimum of six distinct types of metals that play critical roles in fundamental life processes. These essential metals constitute the metallome, which encompasses both organic and inorganic forms of metals within the cell. Alterations in the metallome have significant implications for the physiological functions of plants, impacting various biological processes (Singh and Verma, 2018).

BENEFICIAL PROPERTIES OF NANOFORMS

The field of nanotechnology has experienced rapid growth as an emerging industry, driven by recent advancements in science and technology. These developments have enabled the production of materials with diverse shapes and sizes, including those in the nano-scale range. Such progress serves as a foundation for further innovation, facilitating the design of materials with distinct properties tailored for specific applications (Khot *et al*., 2012). Nanomaterials and nanoparticles (NPs), characterized by their small size typically below 100 nm, form a colloidal particle system that has garnered significant interest in chemical and biological applications. These materials exhibit a unique structure and possess adjustable physicochemical and biological properties, including electrical and thermal conductivity, light absorption, catalytic activity, and antimicrobial capabilities. As a result, they outperform their larger counterparts, offering enhanced performance in various domains (including chemistry and biology). The properties of these nanomaterials can exhibit versatility that is contingent upon their size and shape. Factors such as dissolution, surface reactivity, and aggregation states profoundly influence the fate, lifespan, behavior, and interactions of nanomaterials within various environments. These interactions can often lead to complex global effects.

Nanoscale metals and metal oxides can be naturally present in the environment, either formed by biological entities or as a result of human activities. Additionally, they can be deliberately produced through various methods, collectively known as engineered nanomaterials. These manufacturing approaches encompass chemical, physical, and biological techniques such as chemical reduction, photochemical methods, microwave processing, laser ablation, and grinding (Fig. 1). However, the frequent use of toxic and costly chemicals in chemical and physical synthesis limits their application in everyday life, human health, and agricultural contexts. Consequently, biogenic methods utilizing microbial or plant sources have emerged as promising alternatives for NP production. The rapid advancement in synthesis procedures has led to a significant increase in the manufacture of nanomaterials with desired properties (Gebre & Sendeku, 2019). Nanometals exhibit a core structure composed of inorganic metal or metal oxide, typically enveloped by a thin oxide layer. These materials can be synthesized in various morphologies, including nanoparticles (NPs), nanofibers, nanowires, nanotubes, or nanosheets, each possessing unique and promising attributes. These features include size-dependent qualities, a high surface-to-volume ratio, specific surface plasma resonance, enhanced optical and magnetic properties, and improved antimicrobial activity (Jagadish *et al*., 2018). Due to their reduced size and increased surface area, nanomaterials exhibit distinct characteristics that are often novel and diverge significantly from those observed in the bulk material or at the micro- or macroscopic scale. Additionally, the interactions between molecules within nanomaterials undergo changes, further contributing to their distinctive attributes. These properties are not typically exhibited by the material in its ionic form.

The physicochemical characteristics of nanoparticles (NPs) are influenced by various factors, including their size, morphology, and the nature of the capping materials that cover their surfaces (Rónavári *et al*., 2017). Consequently, the selection of appropriate synthesis methods, along with suitable reducing and stabilizing agents, is crucial to achieve desired particle properties. Metal NPs possess high reactivity and tend to rapidly react with oxygen or biomolecules in biological systems, necessitating surface modifications to prevent aggregation. These modifications involve the use of stabilizing agents, coatings, or functionalization techniques (e.g., with oleic acid, sodium citrate, polymers, or biomolecules). Such approaches promote NP dispersion and ensure a uniform particle size distribution. In the biosynthesis of NPs, various biomolecules such as proteins, polysaccharides, and peptides have been employed. These biomolecules interact with the NPs and can adsorb onto their surfaces, forming a biomolecular corona. This corona acts as an organic complex that enhances NP stability and significantly influences the properties, behavior, and responses of NPs in both environmental and biological contexts. For instance, it can lead to enhanced particle release and reduced toxicity. Consequently, by incorporating different biomolecules during NP synthesis, it becomes possible to design and control the characteristics and fate of metal NPs according to specific requirements (Bélteky *et al*., 2021).

AGRICULTURAL POTENTIAL OF NANOFORMS OF ESSENTIAL METALS

Nano forms of essential metals hold significant agricultural potential due to their unique properties and potential applications. These nanomaterials have the ability to enhance nutrient availability, improve plant growth and development, increase crop yields, and contribute to sustainable agriculture. Nano forms of essential metals can be engineered to enhance the solubility and availability of nutrients in the soil. They can encapsulate essential micronutrients and deliver them to plants in a

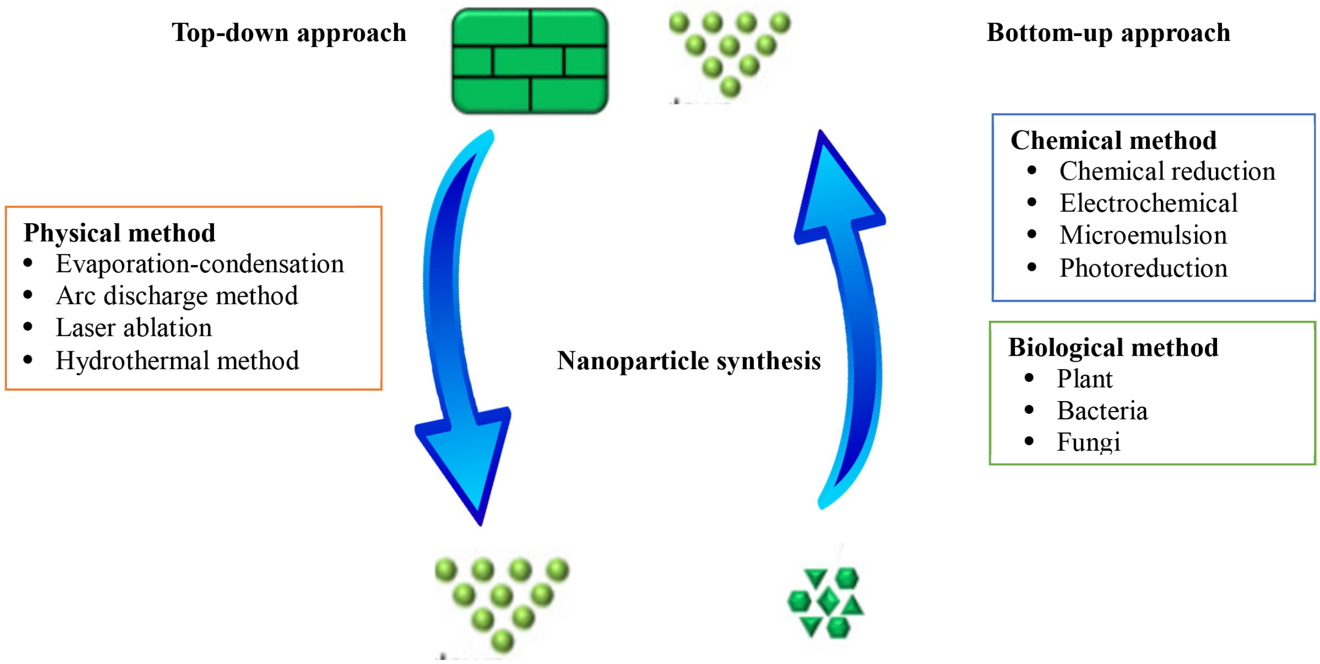

Figure 1: Synthesis of nanoparticles

controlled manner. These nanomaterials can bypass common nutrient limitations in the soil, such as nutrient immobilization or inadequate root uptake, and improve nutrient absorption by plant roots (Kolbert *et al*., 2022). Nanomaterials can be designed as controlled-release systems for essential metals. They can slowly release nutrients over time, ensuring a steady supply to the plants and minimizing nutrient losses through leaching or volatilization. Controlled-release nanomaterials can improve nutrient use efficiency and reduce the need for frequent fertilizer applications (Okey-Onyesolu *et al*., 2021). For enhancing plant growth and development nano forms of essential metals influence various physiological processes. They can modulate hormone levels, promote seed germination, enhance root development, and improve nutrient assimilation. These effects can lead to overall plant vigor, increased biomass, and improved crop productivity (El-Saadony *et al*., 2021). Nanomaterials can be utilized for disease and pest management in agriculture. Nano forms of essential metals can exhibit antimicrobial properties, effectively inhibiting the growth and activity of pathogens in the soil and on plant surfaces. Additionally, they can serve as carriers for targeted delivery of pesticides or antimicrobial agents, minimizing their environmental impact and maximizing their efficacy (Hoang *et al*., 2022; Badawy *et al*., 2021). Essential metal nanoparticles have shown potential in improving plant tolerance to abiotic stresses such as drought (Mazhar *et al*., 2022), salinity (Ye *et al*., 2020), and heavy metal toxicity (Rizwan *et al*., 2019). They can act as stress protectants by mitigating oxidative damage, regulating water balance, and enhancing stress response mechanisms. The use of nanomaterials can help plants adapt to adverse environmental conditions and maintain productivity under challenging circumstances. Nano forms of essential metals have the potential to reduce environmental pollution associated with conventional agricultural practices. By enhancing nutrient use efficiency and reducing the need for excessive fertilization, nanomaterials can minimize nutrient runoff and leaching, thereby reducing water pollution and eutrophication risks (Kalia & Kaur, 2019). Furthermore, targeted delivery systems can reduce the quantity of agrochemicals required, minimizing their impact on ecosystems and non-target organisms. Essential metal nanoparticles can be used as seed coatings to enhance seed germination, early seedling growth, and establishment. These coatings can provide essential nutrients and growth-promoting compounds to the developing seedling, resulting in improved vigor, uniformity, and survival rates (Zhao *et al*., 2021). Additionally, nanomaterials can act as carriers for bioactive substances, such as plant growth regulators or beneficial microorganisms, further enhancing seedling performance. The use of nano forms of essential metals enables precision agriculture practices. Nanosensors can be utilized to monitor soil moisture, nutrient levels, and other environmental parameters in real-time, allowing for precise and targeted management decisions (Raj *et al*., 2022). This helps optimize resource utilization, reduce environmental impacts, and maximize crop productivity. Nanomaterials can be employed for controlled-release of pesticides, minimizing their off-target effects and improving their efficacy. By encapsulating pesticides within nanoparticles, their release can be regulated, extending their activity and reducing the need for frequent applications (Perlatti *et al*., 2013). This approach enhances pest management strategies while reducing chemical inputs and minimizing environmental risks. Nano forms of essential metals find applications in hydroponics and aquaponics systems, where plants are grown in nutrient-rich water (Maluin *et al*., 2021). Nanomaterials can provide essential nutrients to the plants in a soluble and readily available form. Additionally, they can improve water quality by adsorbing and immobilizing excess nutrients, heavy metals, or harmful compounds, ensuring a healthy and productive growth environment for plants. Nano forms of essential metals can influence plant-microbe interactions, including symbiotic relationships with beneficial microbes such as mycorrhizal fungi or nitrogen-fixing bacteria (Ameen *et al*., 2021). These nanomaterials can enhance microbial colonization, nutrient exchange, and overall plant-microbe communication, resulting in improved nutrient acquisition, disease resistance, and plant health. Nano forms of essential metals can contribute to the preservation and protection of harvested crops. They can be used as coatings or packaging materials with antimicrobial properties, inhibiting the growth of spoilage microorganisms and extending the shelf life of agricultural produce (Nair *et al.*, 2020). This approach reduces post-harvest losses and enhances food safety.

Nano forms of essential metals offer immense agricultural potential by improving nutrient management, soil health, plant growth, pest control, and resource efficiency. Their utilization can lead to sustainable agricultural practices, increased crop yields, and reduced environmental impacts. However, it is important to continue research, regulatory oversight, and responsible deployment to ensure their safe and effective integration into agricultural systems.

IMPACTS OF NANOFORMS OF ESSENTIAL METALS ON SOIL HEALTH

Nanoforms of essential metals may exhibit increased reactivity and bioavailability compared to their bulk counterparts. If released in high concentrations, they can potentially accumulate in the soil, leading to elevated metal levels and soil toxicity (Tourinho *et al.*, 2012). This can have detrimental effects on soil microorganisms, beneficial soil organisms, and plant growth. Excessive use or accumulation of nanomaterials in the soil can alter soil structure and stability (Batley *et al.*, 2013). Nanoparticles may interact with soil particles and organic matter, affecting soil aggregation and pore structure (Bayat *et al.*, 2019). This can result in reduced water infiltration, increased surface runoff, and compromised soil aeration, ultimately impacting plant growth and nutrient availability. The soil microbiome plays a crucial role in soil fertility and nutrient cycling. Nanoparticles can have adverse effects on soil microorganisms, disrupting microbial communities and impairing their functions (Kolesnikov *et al.*, 2021). Changes in microbial diversity and activity can affect nutrient availability, organic matter decomposition, and overall soil health. Some nanomaterials have the potential to persist in the environment for extended periods. If nanomaterials are not effectively degraded or transformed, their accumulation over time can lead to long-term environmental impacts (Wiesner *et al.*, 2006). The persistence of nanoparticles in the soil may affect soil biota and potentially enter the food chain, raising concerns about their ecological consequences. Nanoparticles can exhibit greater mobility in the soil compared to bulk materials. This increased mobility raises the possibility of nanoparticle transport through soil pores and their subsequent movement to groundwater or surface water bodies (Bennett *et al.*, 2010). If nanomaterials reach water sources, they may pose a risk of contamination and potentially affect aquatic ecosystems. Nanoforms of essential metals may interact with non-target organisms in the soil ecosystem. Their potential effects on beneficial insects, earthworms, and other soil-dwelling organisms are not yet fully understood (Singh & Gurjar, 2022). Unintended ecological consequences can arise, disrupting ecological balances and causing cascading effects on soil health and ecosystem functioning. The application of nanomaterials in high concentrations or without proper dosage control can lead to nutrient imbalances in the soil. For example, excessive use of nanoparticles containing essential metals may result in nutrient toxicity, inhibiting plant growth and causing nutrient imbalances in the soil (Das *et al.*, 2022). This can negatively impact soil fertility and nutrient cycling processes. Some nanomaterials, particularly those with a high surface area, can influence soil pH. Their interactions with soil components can lead to pH shifts, potentially affecting the availability and uptake of nutrients by plants (Bakshi & Kumar, 2021). Soil pH plays a crucial role in nutrient solubility and microbial activity, and significant alterations can disrupt soil chemical processes and nutrient availability. The potential ecotoxicological effects of nanoforms of essential metals on soil organisms and other non-target organisms are still not fully understood. While some studies indicate potential negative impacts on soil microorganisms, earthworms, or beneficial insects, more research is needed to comprehensively assess the ecological consequences of prolonged exposure to nanomaterials in the soil environment. The use of nanomaterials in agriculture poses regulatory challenges. Due to their unique properties, nanomaterials may require specific regulations and guidelines to ensure their safe use. Developing effective regulatory frameworks and standards that address the potential risks associated with nanoforms of essential metals can be complex and require ongoing evaluation and adaptation. To minimize these negative impacts, it is important to conduct thorough risk assessments and adopt responsible practices when using nanoforms of essential metals in agriculture. This includes adhering to recommended application rates, considering the specific characteristics of nanomaterials, and monitoring their effects on soil health and ecosystem integrity.

CONCLUSION

nanoforms of essential metals possess significant agricultural potential, offering opportunities for improved nutrient management, enhanced crop productivity, and targeted delivery of agrochemicals. They can contribute to precision agriculture, seed enhancement, soil remediation, and sustainable crop protection practices. However, it is crucial to acknowledge and address the potential negative impacts on soil health and the environment. Soil toxicity, impaired soil structure, disruption of the soil microbiome, and the potential for environmental persistence and contamination are among the concerns associated with the use of nanomaterials. Nutrient imbalances, altered soil pH, and unknown ecotoxicological effects further highlight the need for cautious implementation and thorough risk assessments.

Ensure the safe and responsible integration of nanoforms of essential metals into agricultural systems, it is vital to establish robust regulatory frameworks, adhere to recommended dosage and application practices, and conduct ongoing research to better understand their effects on soil health and ecosystem dynamics. Collaboration between scientists, policymakers, and agricultural stakeholders is crucial in addressing the potential risks, developing guidelines for their use, and promoting sustainable agricultural practices. By striking a balance between harnessing the agricultural potential of nanoforms of essential metals and minimizing their adverse effects, we can unlock their full potential as valuable tools for achieving efficient and environmentally sustainable agricultural systems. Continued research, monitoring, and responsible deployment will pave the way for the safe and effective utilization of nanoforms of essential metals in agriculture, ultimately contributing to global food security and the preservation of our natural resources.

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