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Nano-sized Metal Oxide Fertilizers for Sustainable Agriculture: Balancing Benefits, Risks, and Risk Management Strategies

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Abstract

This critical review comprehensively analyses nano-sized metal oxide fertilizers (NMOFs) and their transformative potential in sustainable agriculture. It examines the characteristics and benefits of different NMOFs, such as zinc, copper, iron, magnesium, manganese, nickel, calcium, titanium, cerium, and silicon oxide nanoparticles. NMOFs offer unique advantages such as increased reactivity, controlled-release mechanisms, and targeted nutrient delivery to address micronutrient deficiencies, enhance crop resilience, and improve nutrient efficiency. The review underscores the essential role of micronutrients in plant metabolism, crop growth, and ecosystem health, highlighting their importance alongside macronutrients. NMOFs present significant benefits over traditional fertilizers, including enhanced plant uptake, reduced nutrient losses, and decreased environmental impact. However, the review also critically examines potential risks associated with NMOFs, such as nanoparticle toxicity and environmental persistence. A comparative analysis of different metal types used in nanofertilizers is provided, detailing their primary advantages and potential drawbacks. The review emphasizes the need for cautious management of NMOFs to ensure their safe and effective use in agriculture. It calls for comprehensive research to understand the long-term effects of NMOFs on plant health, soil ecosystems, and human health. By integrating insights from material science, plant biology, and environmental science, this review offers a holistic perspective on the potential of NMOFs to address global food security challenges amid resource constraints and climate change. The study concludes by outlining future research directions and advocating for interdisciplinary collaboration to advance sustainable agricultural practices and optimize the benefits of NMOFs.

Keywords

Nano-sized metal oxide fertilizers, Sustainable agriculture, Micronutrient management, Controlled-release, Environmental impact, Risk management, Life Cycle Analysis

Introduction

Agriculture has dramatically evolved from the ancient practices of civilizations like the Egyptians, Greeks, and Romans, who relied on organic resources such as animal manure, crop rotation, and leguminous plants to enrich soil and support crop growth.¹ These traditional methods aimed to supply essential micronutrients and maintain soil fertility. However, the early 20th century brought a revolutionary change with the advent of the Haber-Bosch process, leading to the widespread use of ammonia-based fertilizers and sparking the Green Revolution. The mass production of macronutrient fertilizers, particularly phosphorus and potassium, transformed agricultural practices, resulting in a staggering increase in global crop yields and food production, soaring from 500 million tons in 1960 to over 2.5 billion tons by 2015. Despite these advancements, the focus on macronutrients has often overshadowed the critical role of micronutrients such as zinc, iron, and manganese in plant growth and development.² Intensive agricultural practices have led to the depletion of these essential micronutrients in soils, raising significant concerns for modern farming systems. The deficiency of micronutrients not only hampers agricultural productivity but also impacts the nutritional quality of crops, posing a global public health challenge.³ Approximately 2 billion people worldwide suffer from micronutrient deficiencies, resulting in compromised immune function, impaired cognitive development, and increased vulnerability to diseases.^{4,5} Addressing soil micronutrient depletion is thus imperative to maintain agricultural productivity, ensure long-term food security, and improve global health.

Traditional fertilizers have largely focused on macronutrients, neglecting the balanced nutrient management required for optimal crop growth. This oversight has led to significant inefficiencies in nutrient management, with several critical gaps evident in current agricultural practices. Conventional fertilizers primarily supply macronutrients, often leading to an imbalance of essential micronutrients in the soil, which contributes to soil degradation,

reduced soil fertility, and the depletion of vital micronutrients necessary for plant health. Furthermore, traditional fertilizers are associated with significant environmental issues, including nutrient runoff, leaching, and eutrophication of water bodies, leading to severe environmental pollution and ecosystem disruption. The bulk application of conventional fertilizers often results in inefficient nutrient utilization by plants, with a substantial portion of these nutrients lost to the environment rather than being absorbed by the plants, leading to lower nutrient use efficiency and increased input costs for farmers. Traditional fertilizers also lack precision in nutrient delivery, unable to provide nutrients at the specific time and location within the plant where they are most needed, resulting in suboptimal growth and productivity. The deficiency of micronutrients in agricultural produce due to imbalanced fertilization practices directly impacts human health, as crops grown in micronutrient-depleted soils have lower nutritional value, contributing to widespread micronutrient deficiencies in the human population.

Nano-sized metal oxide fertilizers (NMOFs) represent a promising solution to these challenges. Leveraging the unique properties of nanoparticles, NMOFs offer several advantages over traditional fertilizers, including increased reactivity, controlled-release mechanisms, and targeted nutrient delivery. These properties enable NMOFs to provide essential micronutrients more efficiently, improving plant uptake and reducing nutrient losses. NMOFs can significantly enhance nutrient use efficiency by providing a controlled and sustained release of nutrients, minimizing losses due to leaching and runoff, and ensuring that a higher proportion of applied nutrients are available for plant uptake. The nanoscale size of NMOFs allows for precise nutrient delivery to specific plant tissues and cellular structures, optimizing nutrient utilization, enhancing plant growth, and improving crop yields. By reducing nutrient losses and improving nutrient use efficiency, NMOFs can mitigate the environmental impact of fertilization practices, reducing the risk of water pollution and

promoting sustainable agricultural practices. NMOFs are particularly effective in addressing micronutrient deficiencies in soils and crops, with their enhanced reactivity and bioavailability ensuring that essential micronutrients like zinc, iron, and manganese are efficiently delivered to plants, thereby improving the nutritional quality of agricultural produce. Despite their potential benefits, the application of NMOFs in agriculture is still in its early stages, and comprehensive research is needed to fully understand their long-term effects on plant health, soil ecosystems, and human health. It is crucial to develop strategies for the safe and effective use of NMOFs, addressing potential risks such as nanoparticle toxicity and environmental persistence.

This review addresses the existing research gap by providing a detailed analysis of the benefits of various NMOFs, including zinc, copper, iron, magnesium, manganese, nickel, calcium, titanium, cerium, and silicon oxide nanoparticles. It explores their potential to enhance crop resilience, nutrient efficiency, and sustainable farming practices. This review critically examines the challenges and concerns associated with NMOFs, such as potential toxicity and environmental risks, and proposes strategies for optimizing their safe use in agriculture. The novelty of this review lies in its comprehensive approach to evaluating NMOFs within the context of sustainable agriculture.

The Crucial Role of Micronutrients in Sustaining Plant Growth and Ecosystem Health

While macronutrients drive overall growth, micronutrients like iron, manganese, and zinc, though needed in smaller quantities, profoundly influence plant metabolism, crop growth, and overall yield.⁶ Orchestrating essential physiological processes, micronutrients like iron, zinc, copper, manganese, boron, and molybdenum, alongside trace elements such as sodium, vanadium, cobalt, selenium, and silicon, regulate critical functions including photosynthesis, enzyme activation, nitrogen fixation, and hormone regulation.^{7,8} Ensuring a precise nutrient

balance is vital for promoting robust plant growth, as insufficient levels of micronutrients can impede crop productivity and nutritional quality, resulting in stunted growth, heightened vulnerability to pests and diseases, and diminished yield. The identification of specific deficiency symptoms poses a challenge due to their multifaceted effects.⁹ For instance, a single symptom such as stunted growth may indicate deficiencies in multiple micronutrients. Moreover, many deficiencies exhibit similar visual cues; for example, leaf chlorosis (yellowing) can be symptomatic of deficiencies in iron, magnesium, nitrogen, and sulfur.

Micronutrients serve as the foundation of ecosystem health, driving critical biochemical reactions that sustain diverse plant species and support nutrient cycling. From facilitating photosynthesis to catalyzing enzyme activity, micronutrients are essential for ecosystem resilience. They promote the growth of diverse plant species and establish complex ecological communities, from forest canopies to grassland undergrowth. Moreover, micronutrients play a vital role in nutrient cycling, facilitating the breakdown of organic matter and recycling essential nutrients. Interactions with soil microorganisms contribute to organic material decomposition, releasing vital nutrients into the soil for plant uptake, as well as critical symbiotic processes such as biological nitrogen fixation.¹⁰ Micronutrients are essential for supporting not only plant growth but also ecosystem function, playing a vital role in maintaining the delicate equilibrium of natural ecosystems and fostering biodiversity. Appreciating their diverse functionality is imperative for advancing agricultural sustainability, a subject explored in this review.

Development of nanofertilizers in agricultural applications

Elemental nanomaterials have several unique attributes that have profound implications across various sectors, including agriculture. Importantly, the development of nanofertilizers derived from conventional counterparts signifies a monumental leap forward in agricultural

techniques, offering innovative solutions to many of the sustainability concerns that plague conventional agriculture.¹¹ These nanoscale fertilizers showcase superior nutrient delivery mechanisms, enhancing the efficiency of nutrient uptake by plants while substantially reducing environmental foot prints compared to traditional fertilizers.¹² This paradigm shift towards nanofertilizers holds significant promise for promoting sustainable agricultural practices, as they can play a crucial role in mitigating environmental degradation and conserving vital resources, thereby advancing crop productivity and ensuring long-term food security in today's rapidly changing agricultural landscape.

Within the realm of nanofertilizers, a diverse array material exists, each characterized by its unique composition, function, and mechanism of nutrient delivery. From nanoscale macronutrient fertilizers to nano-coated and nano-encapsulated varieties, nanofertilizers offer a spectrum of options that can be tailored to meet specific agricultural needs.^{13,14,15} These nano-scale formulations, with their exceptional reactivity and increased bioavailability, facilitate enhanced nutrient uptake by plants, directly translating into improved plant performance and yield. Moreover, the utilization of nanofertilizers contributes significantly to sustainability efforts in agriculture by reducing the volume of fertilizers required, mitigating the risks associated with over-fertilization, and implementing controlled- or even responsive-release systems that outperform traditional fertilizers in terms of efficiency and environmental impact.^{16–20} By promoting cost-effectiveness and environmental preservation, nanofertilizers emerge as powerful tools in the quest for sustainable agricultural practices.

The types and benefits of nano-scale metal oxide fertilizers

Nano-scale metal oxides (NMOs) are typically produced from metal precursors through a synthesis process involving the addition of oxidizing or precipitation compounds.²¹ Generally, NMO particles have unique physicochemical properties due to their small size and

high density of corner or edge surface sites, which is a distinct characteristic of metal nanoparticles. NMOs, such as titanium dioxide (TiO_2) and zinc oxide (ZnO), are commonly produced on a large scale for applications in the fabrication of nanoscale electrical circuits and semiconductors, leveraging their remarkable electrical and conductive properties.²² These nanoparticles have been pivotal in driving forward numerous breakthroughs in chemistry, physics, and materials science, including advancements in nanoelectronics, sensors, and energy storage devices.^{23,24} However, NMOs are finding new applications in precision agriculture, where they are used directly as nutrient sources or are utilized to deliver hormones, pesticides, herbicides, and fertilizers with enhanced efficiency and precision.^{17,25} For instance, nanoscale formulations of herbicides encapsulated within metal oxide nanoparticles have shown promise in targeted weed control, minimizing environmental impact and improving crop yields.²⁶ Similarly, nanocoated fertilizers incorporating metal oxides exhibit controlled release properties, ensuring optimal nutrient delivery to plants while reducing nutrient runoff and soil contamination. These innovative applications underscore the multifaceted role of metal oxide nanoparticles in modern technology and agriculture, driving forward sustainable and efficient solutions for diverse societal challenges. The application of NMOs in agriculture remains in its nascent phase and a number of challenges remain. However, their utilization as additives in fertilizers has demonstrated promising results in enhancing plant growth and yield across diverse crop varieties, including rice, wheat, barley, grass pea, tomato, celery, and eggplant (**Table 1 & 2**).^{15,27–31} Notably, titanium, zinc, and iron oxides have already been patented as additives in commercial fertilizers in several countries, including the USA.^{32–33} Furthermore, NMOs have been the subject of numerous research studies exploring their potential as compounds for pest control or indirectly as stimulators of plant health that enables biotic stress resistance.²⁵

Traditional inorganic fertilizers often suffer from suboptimal nutrient delivery and utilization due to reactivity with soil or other environmental components, as well as limited efficiency in plant nutrient uptake. However, the effectiveness of nutrient delivery is influenced by various factors, including fertilizer types, soil conditions, application methods, and plant requirements. These fertilizers typically exist in bulk forms, such as granules, salts, pellets, or liquid formulations, and primarily contain essential nutrients crucial for plant growth, such as NPK formulations. In contrast, nanomaterials offer larger surface areas compared to their bulk counterparts, facilitating efficient nutrient delivery and translocation within plants. Compelling evidence indicates that even micronutrients, which are typically immobile in plants, can be internally translocated when delivered in nanoscale form.³⁴ This advantage enables greater in planta nutrient translocation, thereby promoting the growth of critical plant components like flowers and buds, without solely relying on constant absorption from external sources.

Zinc oxide nanoparticles (ZnO-NPs)

Zinc (Zn) is crucial for numerous plant physiological processes, including enzyme activation, photosynthesis, and hormone regulation. It serves as a cofactor for over 300 enzymes involved in essential functions like DNA replication, protein synthesis, and carbohydrate metabolism.³⁵ Despite the small amount of zinc required (0.5–2 μM), it plays a significant role in regulating plant hormones such as auxin, which influence stem elongation, root growth, and bud development. Zinc also stabilizes cell membranes, helping plants withstand environmental stresses and enhancing their defense mechanisms against fungal and bacterial infections.³⁶ However, zinc deficiency, particularly in calcareous and alkaline soils, can limit crop productivity and nutritional quality, which poses public health concerns by affecting human nutrition.³⁷

Zinc oxide nanoparticles (ZnO-NPs), due to their nanoscale size and high solubility, greatly enhance zinc availability in the soil or on plant leaves, leading to more efficient absorption. When ZnO-NPs dissolve in the soil, they release Zn^{2+} ions, which are absorbed by plant roots through specific zinc transporters located in the root cell plasma membranes. These nanoparticles are significantly more effective than bulk zinc fertilizers because their high surface area ensures a more consistent and prolonged release of Zn^{2+} ions, resulting in better root absorption. The absorption of Zn^{2+} is facilitated by ZIP (Zinc/Iron-regulated transporter-like Protein) transporters, which become more active in zinc-deficient conditions.³⁸ These transporters, part of the ZIP family, play a vital role in zinc and other metal ion uptake, including manganese (Mn^{2+}), iron (Fe^{2+}), cadmium (Cd^{2+}), and others, thus contributing to metal homeostasis in plants. Once absorbed, Zn^{2+} ions are rapidly translocated to shoots and leaves through the xylem and are involved in critical biochemical processes, such as serving as cofactors for enzymes like superoxide dismutase (SOD), which neutralizes reactive oxygen species (ROS) and protects plants under stress conditions such as drought, salinity, and extreme temperatures. ZnO-NPs, typically ranging in size from 15 nm to over 100 nm, also outperform traditional zinc sources by improving nutrient absorption, plant growth, stress resistance, and nutrient utilization, with studies showing improvements in plant growth by 30-40% and enhanced stress resilience.^{29,39,40} These nanoparticles are particularly beneficial in regions with zinc-deficient soils, where traditional zinc fertilizers fail to provide sufficient bioavailable zinc.^{39,41}

ZnO-NPs differ from traditional zinc sources primarily due to their nanoscale size, which allows for enhanced penetration into plant cells via stomatal openings and root epidermal tissues. Once in the plant system, ZnO-NPs dissolve into zinc ions (Zn^{2+}), which are then transported through the xylem to various tissues, where they participate in critical biochemical processes. One of the most significant pathways influenced by zinc is the

antioxidant defense system, where zinc ions act as cofactors for superoxide dismutase (SOD), an enzyme that mitigates oxidative stress by neutralizing reactive oxygen species (ROS).⁴² This is particularly important under abiotic stress conditions such as drought, salinity, and extreme temperatures.

Recent studies demonstrate that ZnO-NPs can enhance photosynthetic efficiency by regulating the biosynthesis of chlorophyll. For example, in a controlled study on maize (*Zea mays*),⁴³ the foliar application of ZnO-NPs at 30 mg/L led to a significant increase in chlorophyll content, improving the plant's ability to capture light and convert it into energy, thereby boosting overall growth and yield by approximately 20%. The increased chlorophyll production is directly tied to the higher bioavailability of zinc, which is a crucial element in the chlorophyll biosynthesis pathway. ZnO-NPs are superior to traditional zinc fertilizers not only in terms of bioavailability but also in terms of their ability to be more efficiently translocated within the plant. Bulk zinc fertilizers, such as zinc sulfate (ZnSO_4), typically suffer from poor mobility in soils, especially in alkaline soils, where zinc precipitates as insoluble forms, reducing its uptake by plants. ZnO-NPs, on the other hand, maintain their solubility even in high pH soils due to their unique physicochemical properties. In a study on wheat (*Triticum aestivum*), the application of ZnO-NPs at 100 mg/L improved grain zinc content by 30% compared to traditional zinc sulfate applications.^{44–47}

ZnO-NPs not only enhance plant growth but also provide antimicrobial protection. Zinc plays a role in strengthening plant cell walls, making it more difficult for pathogens to invade. ZnO-NPs have been shown to exhibit significant antibacterial and antifungal properties, with studies indicating their effectiveness against major plant pathogens such as *Botrytis cinerea*, *Fusarium oxysporum*, and *Ralstonia solanacearum*.^{44, 48, 49} These antimicrobial effects are thought to be driven by the generation of ROS upon interaction with microbial cells, leading to cell membrane disruption and subsequent cell death. For instance, in tomato plants, ZnO-

NPs at 100 mg/L significantly reduced bacterial wilt incidence caused by *Ralstonia solanacearum*, while also enhancing the plant's antioxidant enzyme activity, thereby improving overall resistance to the disease. Moreover, ZnO-NPs can enhance abiotic stress tolerance, especially against drought and salinity. In wheat, ZnO-NPs increased the expression of stress-related transcription factors, such as DREB (Dehydration-Responsive Element Binding) and WRKY genes, which are key players in the plant's response to environmental stresses.^{30,50–54}

Despite the many benefits of ZnO-NPs, there are growing concerns about their long-term environmental impact. One of the main issues is the potential for zinc accumulation in soils, particularly with repeated use. High concentrations of ZnO-NPs can lead to phytotoxicity, characterized by reduced plant growth and altered microbial communities in the rhizosphere.^{55,56} This is particularly problematic in sandy soils or soils with low organic matter, where ZnO-NPs are more likely to leach into groundwater or accumulate in the soil profile. Studies have shown that concentrations of ZnO-NPs above 500 mg/L can negatively impact the growth of soil microorganisms responsible for nutrient cycling, potentially leading to a decline in soil fertility over time.⁵⁷

Copper Oxide Nanoparticles (CuO-NPs)

Copper oxide nanoparticles (CuO-NPs) have garnered significant attention in agricultural research due to their broad applications in enhancing plant growth and controlling plant diseases. Copper (Cu) is an essential micronutrient that plays a vital role in several physiological processes, including photosynthesis, respiration, protein synthesis, and stress defense. Copper is critical for both the photosynthetic and respiratory electron transport chains. In photosynthesis, copper acts as a cofactor for plastocyanin, which facilitates electron transfer between photosystem II and photosystem I, ensuring efficient energy

production.⁵⁸ In respiration, copper is a crucial component of cytochrome c oxidase in the mitochondrial electron transport chain, playing a key role in ATP synthesis. Copper also participates in ethylene signaling, cell wall metabolism, and the biogenesis of molybdenum cofactor.⁵⁹

CuO-NPs, with sizes ranging from 9 nm to 75 nm and morphologies that include spherical and rod-shaped forms, exhibit diverse mechanisms of action that improve various aspects of plant physiology.^{31,60,61} First and foremost, CuO-NPs enhance photosynthesis by facilitating greater copper availability,^{62,63} which boosts plastocyanin activity in the electron transport chain, leading to increased energy production and chlorophyll synthesis. The high solubility and bioavailability of copper ions from CuO-NPs allow for more efficient uptake through COPT transporters, which are specialized for Cu^+ ion absorption in plant roots. These nanoparticles release copper ions more effectively than bulk copper fertilizers, ensuring a steady and prolonged supply of copper for nutrient uptake and plant growth.^{64,65} This leads to better absorption through both the roots and foliage. Additionally, CuO-NPs enhance the antioxidant defense system by activating SOD and other copper-dependent enzymes, mitigating oxidative damage under stress conditions such as drought, salinity, and pathogen attacks.^{66,67} CuO-NPs also regulate gene expression, influencing key pathways related to nutrient acquisition, growth, and secondary metabolite production. They have been shown to improve seed germination, enhance early seedling growth, and promote the production of insecticidal proteins in transgenic crops.

Moreover, CuO-NPs exhibit strong antimicrobial properties, effectively inhibiting a range of bacterial and fungal pathogens that harm plants.⁶⁸⁻⁶⁹ This provides an additional layer of protection against diseases, helping plants to maintain health and productivity. CuO-NPs also enhance water use efficiency by improving root architecture and regulating stomatal

behavior, which allows plants to make better use of available water, especially under water-limited conditions.^{70,71,62,63} They also positively impact the microbial community in the rhizosphere by promoting the growth of beneficial bacteria that enhance nutrient availability and disease resistance. Despite these numerous advantages, there is still a notable lack of long-term studies that investigate the impact of CuO-NPs on plant and soil health. While short-term studies highlight the positive effects of CuO-NPs on plant growth, nutrient uptake, and stress tolerance, the long-term consequences of their application remain unclear. There is a need for comprehensive studies that assess the potential accumulation of CuO-NPs in the soil and their effects on soil microbial populations and the availability of other micronutrients. Such research is crucial for understanding the nutrient profiling of plants treated with CuO-NPs, including their effects on micronutrient balance and overall nutritional content in both foliar and soil applications.

Iron oxide nanoparticles (FeO-NPs)

Iron (Fe), similar to zinc and copper, plays a multifunctional role in plant physiology and soil health, profoundly influencing crop productivity. As a critical component for chloroplast synthesis, iron is essential for photosynthesis, energy, and oxygen production.^{72,73} Iron deficiency hinders chlorophyll synthesis, impairs photosynthesis, and stunts plant growth. Iron is crucial for electron transport within chloroplasts, ATP generation, and serves as a cofactor for enzymes involved in DNA, RNA, protein synthesis, and organic compound metabolism.^{72,74} In nitrogen metabolism, iron facilitates the conversion of nitrate (NO_3^-) into ammonia (NH_4^+), which is vital for amino acid and protein synthesis.⁷⁵ Iron also enhances soil health by increasing microbial enzyme production that breaks down organic matter, releasing nutrients for plant absorption, thereby promoting growth.^{72,76} Iron deficiency in soils can cause iron chlorosis in plants, characterized by leaf yellowing due to insufficient chlorophyll.⁷⁵ The role of iron in soil health is closely linked to human nutrition and

micronutrient deficiencies. Iron is a crucial micronutrient for human health, and its deficiency can lead to severe health complications. According to the World Health Organization (WHO), approximately two billion people worldwide suffer from iron deficiency, making it one of the most prevalent nutrient deficiencies globally. Therefore, maintaining adequate iron levels in soil is essential for ensuring the nutritional quality of food crops and addressing potential deficiencies in human diets. Addressing iron deficiencies is vital for successful crop growth. Iron availability in soil is influenced by pH levels. High-pH (alkaline) soils, usually ranging from 7.5 to 8.5, often restrict iron solubility and accessibility, while low-pH (acidic) soils, with a pH around 6, can enhance iron availability. The optimal range for plants to access iron is slightly acidic to neutral soils, with a pH range of 6.0 to 7.0.⁷⁷ Thus, maintaining optimal pH levels is crucial for iron uptake. Iron supports soil microorganisms, fostering microbial diversity, promoting nutrient cycling, and boosting soil fertility. It participates in redox reactions in soil, affecting nutrient availability and mobility, and influences the soil's capacity to retain and release essential nutrients to plants.⁷⁸ Iron promotes soil aggregation and enhances water infiltration and aeration, creating a conducive environment for robust plant root growth and efficient nutrient absorption.

Iron oxide (Fe_2O_3) nanofertilizers have proven to enhance plant growth and increase crop yield. Compared to traditional iron fertilizers such as iron sulfate, FeO-NPs have demonstrated superior efficacy in improving iron uptake, particularly in iron-deficient soils. Studies have shown that applying FeO-NPs at concentrations ranging from 50 mg/L to 300 mg/L significantly boosts chlorophyll content, enhances photosynthetic efficiency, and increases biomass by over 100% compared to similar concentrations of bulk iron fertilizers.⁷⁹ This enhanced performance is primarily attributed to the nanoparticles' high surface area and increased solubility, which improve the availability of Fe^{2+} ions to plants. FeO-NPs also excel in enhancing crop productivity under stress conditions. For instance, in Canola (*Brassica*

napus), FeO-NP treatment upregulated the expression of iron transporters in the roots, promoting iron uptake even during drought stress.⁸⁰ Iron, as a cofactor for enzymes like catalase and peroxidase, plays a critical role in protecting plants from oxidative damage by breaking down hydrogen peroxide into water and oxygen. Typically existing in soil as Fe^{3+} ions, mainly as ferric oxides, this critical nutrient often has very low bioavailability. The application of FeO-NPs to soil facilitates the release of Fe^{2+} ions, which are more readily assimilated by plants, thereby addressing this nutrient uptake challenge.⁷⁹ FeO-NPs fertilizers offer significant advantages in enhancing overall crop growth and yield, although their effectiveness depends on factors such as crop type and soil conditions.⁸¹ FeO-NPs have shown positive impacts on various crop varieties when administered at appropriate doses. They offer numerous benefits compared to their bulk counterparts, including an extended lifespan in soil, providing a more consistent and adjustable release of iron to plants over time.⁸² However, factors such as soil properties, FeO-NP attributes (coating, size), and environmental conditions greatly affect their durability and release behaviour. Despite these advantages, there remains a notable absence of long-term exposure studies investigating the impact of FeO-NPs on plants and soil. This highlights a critical gap in understanding their potential effects over prolonged periods. Comprehensive investigations into the nutrient profiling of plants treated with FeO-NPs are also necessary to fully evaluate their overall nutritional impact in both foliar and soil applications.

Magnesium oxide nanoparticles (MgO-NP)

Magnesium, like zinc and iron, is a crucial micronutrient for plants, playing vital roles in several physiological processes that are essential for overall plant growth. Some of the key functions of magnesium in plants include:^{83,84} (1) serving as an integral component of chlorophyll, the pigment responsible for plants' green color and their ability to capture sunlight and convert it into energy through photosynthesis; (2) acting as a cofactor for

numerous enzymes involved in metabolic processes, such as protein synthesis, cellular respiration, and carbohydrate metabolism. By activating enzymes like RuBisCO, magnesium helps facilitate more efficient energy production and cellular metabolism, which drives plant growth; and (3) contributing to the strength and stability of plant cell walls.

Magnesium deficiency in plants can lead to a variety of symptoms, including leaf yellowing (chlorosis), stunted growth, and reduced fertility.⁸⁵ In severe cases, it can even result in plant death. Factors contributing to magnesium deficiency include low magnesium levels in the soil, inappropriate soil pH (either too high or too low), and the presence of other nutrients, such as potassium or calcium, which can interfere with magnesium uptake. Magnesium deficiency is particularly common in alkaline or sandy soils, or in soils with high levels of potassium or calcium, which compete with magnesium for absorption. Magnesium ions (Mg^{2+}) from MgO nanoparticles (MgO-NPs) can help mitigate deficiency by regulating ion channels and improving the uptake of other essential nutrients, such as potassium and phosphorus. These nutrients are critical for stomatal regulation, energy transfer, and nutrient transport. Enhanced magnesium availability from MgO-NPs also promotes better root development, increasing root hair formation and improving root architecture, which further supports nutrient and water uptake, ultimately leading to improved plant growth and productivity.

Magnesium oxide nanoparticles (MgO-NPs) have shown strong beneficial impacts on crop growth and soil health.⁸⁶ MgO-NPs enhance soil structure and promote the proliferation of beneficial soil microorganisms, improving soil quality and resulting in enhanced crop growth. These nanoparticles also exhibit antimicrobial properties, effectively controlling harmful phytopathogenic microbes such as *Fusarium verticillioides*, *Bipolaris oryzae*, and *Fusarium fujikuroi* in rice.⁸⁷ Furthermore, MgO-NPs have been reported to control fungal pathogens in

the leaf phyllosphere of tomatoes and protect against bacterial wilt caused by *Ralstonia solanacearum*, a soil pathogen. In tobacco, root irrigation with MgO-NPs provided protection against soil-borne pathogens *Thielaviopsis basicola* and *Phytophthora nicotianae*, significantly reducing disease incidence by over 40% compared to untreated plants. The application of MgO-NPs at appropriate concentrations has been associated with improved soil quality, promoting the growth of beneficial bacterial communities involved in carbon cycling.^{88,89} These findings highlight the dual benefits of MgO-NPs for soil quality enhancement and pathogen control.^{90,91} The increased Mg content in plant tissues suggests effective uptake and translocation by roots, promoting overall plant health. However, there is a need for comprehensive investigations into the long-term effects of MgO-NPs on both plants and soil. Understanding the potential impacts of prolonged exposure to MgO-NPs and conducting nutrient profiling of plants treated with these nanoparticles will provide a more complete evaluation of their overall nutritional impact.

Manganese oxide nanoparticles (MnO-NP)

Manganese (Mn) is an essential micronutrient that plays a vital role in various physiological processes in plants, including photosynthesis, nitrogen assimilation, and protection against oxidative stress. Mn functions as a cofactor in the oxygen-evolving complex of photosystem II, facilitating the production of ATP and NADPH during photosynthesis.^{92,93} It is also critical for nitrogen assimilation, supporting enzymes that convert nitrogen into forms usable for protein synthesis. Mn acts as a cofactor for superoxide dismutase (SOD), an enzyme responsible for detoxifying reactive oxygen species (ROS), thus safeguarding plant cells from oxidative damage. Moreover, Mn is involved in hormone signaling pathways, influencing the biosynthesis and activity of key plant hormones such as auxin, cytokinin, and gibberellin, all of which regulate plant growth and development.^{93,94,95,96} In addition, Mn activates defense-related genes and enzymes, enhancing plant resistance to biotic stresses like pathogens.⁹⁷

Manganese deficiency can lead to detrimental effects on plant growth, such as chlorosis (leaf yellowing), impaired photosynthesis, and stunted development. In soils where Mn availability is limited, particularly in acidic soils where Mn solubility increases and can become toxic, plants experience stress that hampers their physiological functions.⁹⁸⁻⁹⁹ Mn toxicity can result in ROS overproduction, leading to oxidative stress. Plants mitigate these effects by increasing antioxidant activity and storing excess Mn in vacuoles, which act as protective reservoirs to prevent toxicity. The application of manganese oxide nanoparticles (MnO-NPs) has gained interest due to their ability to enhance Mn availability to plants. Limited but promising studies have shown that MnO-NPs improve seed germination, enhance nutrient uptake, and positively influence hormonal and antioxidant profiles. Like traditional forms of Mn, MnO-NPs contribute to photosynthesis, enzyme activation, and ROS scavenging, but they offer additional benefits through their nanoscale size. MnO-NPs provide more controlled release of Mn^{2+} ions, ensuring sustained bioavailability, which can lead to more efficient uptake by roots and translocation to plant tissues.

MnO-NPs offer several advantages over bulk manganese fertilizers such as manganese sulfate (MnSO_4), especially in calcareous or alkaline soils, where manganese availability is limited. In a study on watermelon (*Citrullus lanatus*) seedlings, MnO-NP application at 100 mg/L resulted in a 25% improvement in seed germination rates and an approximate 20% increase in root biomass compared to conventional manganese fertilizers.⁹⁸ This enhanced growth is attributed to the higher bioavailability of manganese from MnO-NPs, which promotes better chlorophyll synthesis and photosynthetic activity. Moreover, MnO-NPs have demonstrated efficacy in reducing disease incidence in crops like tomato and eggplant infected with Fusarium wilt and Verticillium wilt.⁹⁹ In wheat (*Triticum aestivum*), MnO-NPs have shown subtle effects on nutrient acquisition, improving manganese translocation efficiency and resulting in increased nutrient use by plants.¹⁰⁰ MnO-NPs also positively

influence nitrogen metabolism by enhancing the activity of nitrate reductase, an enzyme responsible for converting nitrate into ammonia, a critical step in amino acid and protein synthesis. This was demonstrated in wheat, where MnO-NP application led to a 15% increase in grain yield and improved protein content compared to untreated plants.¹⁰⁰ In tomato (*Solanum lycopersicum*) plants, MnO-NPs applied at 50 mg/L increased SOD activity by 30%, significantly enhancing the plants' tolerance to oxidative stress under drought conditions.⁸⁷ MnO-NPs also provide resistance to fungal pathogens. For example, in eggplant (*Solanum melongena*), MnO-NP application effectively reduced the incidence of *Verticillium* wilt by more than 35% compared to untreated plants, likely due to enhanced plant defense mechanisms.⁸⁸ Overall, MnO-NPs hold great potential for improving crop productivity and quality, offering a safe and eco-friendly solution for seed priming and plant health enhancement in various crops.

Nickel oxide nanoparticles (NiO-NPs)

Nickel is an essential micronutrient for plants, serving as a cofactor for various enzymes, including urease, which is pivotal for nitrogen metabolism and the utilization of urea. As part of the urease enzyme, nickel helps break down urea into ammonium,¹⁰¹ fostering healthy growth and development, particularly in legumes and plants that rely on ureides for nitrogen

Adequate nickel levels support optimal chlorophyll content, enhancing photosynthesis and overall plant growth. Nickel also plays a critical role in pollen grain formation and pollen tube growth, ensuring successful fertilization and seed production.¹⁰² It activates enzymes involved in stress response pathways, enabling plants to better cope with environmental challenges like oxidative stress, heavy metal toxicity, drought, and salinity. This activation enhances antioxidant defences, detoxification processes, osmotic regulation, and cell wall strengthening, aiding plant adaptation and survival under adverse conditions.¹⁰³ The

requirement for nickel in plants is extremely low, and nickel deficiency is correspondingly rare. In higher plants, typical nickel concentrations range from 0.5 to 10 mg/kg dry weight (DW). However, concentrations exceeding 10–50 mg/kg DW (depending on the plant species) can lead to nickel toxicity, causing detrimental effects on plant health.¹⁰⁴

Nickel oxide nanoparticles (NiO-NPs) have been studied for their ability to improve nickel delivery to plants more efficiently. Research indicates that soil application of NiO-NPs enhances urea decomposition, boosts nitrogen-fixing enzyme activity, and improves overall plant productivity. For example, the application of NiO-NPs at a concentration of 50 mg/kg led to a 39% increase in soybean seed yield, a 28% rise in total fatty acid content, and a 19% increase in starch content.¹⁰¹ These improvements can be attributed to the regulatory effects of NiO-NPs on key physiological processes, including photosynthesis, mineral homeostasis, phytohormone regulation, and nitrogen metabolism. Unlike traditional nickel sources like nickel sulfate (NiSO_4), NiO-NPs offer a more prolonged supply of Ni^{2+} ions, which helps in reducing the risks of phytotoxicity.^{105,106} Although no specific nickel transporters have been identified in plants, nickel uptake is thought to occur through non-selective cation transporters, particularly members of the ZIP (ZRT/IRT-like Protein) family. Among these, IRT1 (Iron-Regulated Transporter 1) is notable for its role in the uptake of iron (Fe) but also facilitates the transport of other divalent cations, including Ni, Zn, Co, Cd, and Mn. This suggests that NiO-NPs may be absorbed by plants via similar mechanisms, ensuring efficient nickel uptake and utilization in various biochemical processes.

Despite their benefits, research on NiO-NPs' potential toxicity is limited. Some studies have highlighted that high concentrations of NiO-NPs can reduce soil microbial biomass, soil mineral nitrogen, and plant-available potassium, potentially harming nutrient mineralization and plant nitrogen uptake.^{106,107} NiO-NPs treatment can also decrease chlorophyll,

carotenoid, and sugar levels while increasing stress-related compounds and enzyme activities in plants.^{106, 108} Nickel deficiency in plants can cause symptoms like reduced growth, stunted development, yellowing of leaves, and reduced fertility. Factors contributing to nickel deficiency include low soil nickel levels, inappropriate soil pH, and the presence of other nutrients like zinc and copper that interfere with nickel uptake, as these elements share a common uptake system with nickel.¹⁰⁹ While NiO-NPs hold promise for enhancing plant growth, productivity, and nutritional quality, their application must be carefully managed to mitigate potential toxicity risks and ensure sustainable agricultural practices.

Calcium oxide nanoparticles (CaO-NPs)

Calcium (Ca) is an essential macronutrient required for cell wall formation, enzyme activation, and signal transduction in plants.¹¹⁰ It plays a critical role in maintaining cellular structure, regulating ion transport, and mediating responses to environmental stress. Calcium is particularly important for the development of new tissues, and its deficiency can lead to issues such as blossom end rot in tomatoes and tip burn in leafy vegetables.^{111,112}

Calcium oxide nanoparticles (CaO-NPs) offer a highly efficient means of delivering bioavailable calcium to plants, particularly in acidic soils where calcium availability is often limited. Due to their nanoscale size, CaO-NPs can be absorbed more effectively by plant roots, ensuring a sustained release of Ca^{2+} ions that promote healthy plant growth and development.

CaO-NPs have been shown to be more effective than traditional calcium fertilizers, such as calcium nitrate or calcium carbonate, in improving calcium uptake and enhancing plant growth. In a study on tomato (*Solanum lycopersicum*) seedlings, the application of CaO-NPs at concentrations of 50 mg/L significantly increased stem height and root biomass by 20%

and 25%, respectively, compared to bulk calcium fertilizers.¹⁰⁴ This improvement was due to the increased solubility and bioavailability of Ca^{2+} ions from the nanoparticles. Moreover, CaO-NPs have been found to enhance fruit quality by improving fruit firmness and size, particularly in crops such as cucumbers, tomatoes, and berries. In cucumber plants, the application of CaO-NPs at 100 mg/L increased fruit firmness by 15% and improved fruit shelf life by delaying the onset of post-harvest decay.^{112,113} These benefits are attributed to calcium's role in strengthening cell wall pectin, which provides structural support to the fruit. Calcium is also vital for enhancing a plant's resilience to stress.^{112,114} CaO-NPs have been shown to help plants withstand salinity, drought, and pathogen attacks by regulating ion transport and strengthening cell walls. In a study on barley (*Hordeum vulgare*), CaO-NPs applied at 60 mg/L improved the plant's tolerance to salt stress, reducing sodium uptake by the roots while maintaining calcium levels in the shoots. This helped the plants maintain osmotic balance under high-salinity conditions, improving overall growth.^{111,115} CaO-NPs have been found to play a role in pathogen defense by activating calcium-dependent protein kinases (CDPKs), which are involved in signal transduction pathways that regulate plant responses to pathogen invasion. In tomato plants, the application of CaO-NPs reduced the severity of blossom-end rot caused by calcium deficiency, while also decreasing the incidence of bacterial infections such as *Pseudomonas syringae* pv. tomato, which causes bacterial speck.¹¹⁶ While CaO-NPs are generally considered safe for plant and environmental health, excessive use can lead to calcium toxicity, particularly in soils with high calcium content. Symptoms of calcium toxicity include stunted growth, leaf necrosis, and interference with the uptake of other essential nutrients, such as magnesium and potassium. In soils, over-application of CaO-NPs can lead to alkalinity, which may affect nutrient availability, particularly for micronutrients like iron and zinc. There is also limited research on the long-

term accumulation of CaO-NPs in soils, and more studies are needed to determine their impact on soil structure and microbial activity.

Titanium dioxide nanoparticles (TiO₂-NPs)

Titanium dioxide (TiO₂) is not an essential nutrient; nevertheless, studies have demonstrated that TiO₂-NPs can exert diverse positive impacts on plant growth and development, contingent upon factors such as nanoparticle size, concentration, plant species, and duration of exposure. Several studies have documented favourable outcomes, including enhanced photosynthesis, improved nutrient absorption, and shielding against environmental stressors like ultraviolet (UV) radiation. Titanium dioxide (TiO₂) is commonly used in plants due to its ability to enhance photosynthesis, light absorption, and stress tolerance. TiO₂ nanoparticles (TiO₂-NPs) have a high photocatalytic efficiency, allowing them to interact with light and improve the photosynthetic rate of plants by increasing the absorption of UV and visible light. This enhances the conversion of light energy into chemical energy, particularly in crops grown under suboptimal lighting conditions. Farahi et al. (2023)¹¹⁷ explored the effects of TiO₂-NPs on photosynthetic pigments, biochemical activities, and antioxidant enzymes in Vitex plants (Chaste trees). Different concentrations of nanoparticles (0, 200, 400, 600, and 800 ppm) were sprayed on Vitex plants on the 30th day of the experiment. TiO₂-NPs positively influenced root and shoot dry weight but negatively impacted leaf dry weight. Chlorophyll levels increased with TiO₂NP concentration, while chlorophyll b decreased, and total chlorophyll remained stable. The highest soluble sugar content was observed with the 200-ppm nanoparticle treatment. Proline and soluble protein content remained unaffected. However, foliar application of TiO₂-NPs significantly enhanced antioxidant enzyme activity compared to the control. Overall, the study indicated a beneficial impact of TiO₂-NPs on dry matter production and various antioxidant and biochemical properties of Vitex plants.

In addition to stimulating plant growth, TiO₂-NPs possess potent antimicrobial properties against numerous plant pathogens. For instance, in an in vitro antifungal assay, TiO₂-NPs at a concentration of 0.43 mg per plate effectively controlled *Fusarium solani*, the causative agent of Fusarium wilt disease in potatoes. Moreover, at 0.75 mg per plate, they exhibited efficacy against *Venturia inaequalis*, responsible for Apple scab disease.¹¹⁸ In a study involving Faba Bean plants, foliar application of TiO₂-NPs at a concentration of 150 µM successfully managed *Broad bean stain virus* (BBSV).¹¹⁹ Furthermore, in wheat, effective control of wheat rust caused by *Ustilago tritici* was achieved at a concentration of 0.10 mg/mL in an in vitro antifungal assay.¹²⁰ Additionally, TiO₂-NPs at a concentration of 0.5 mg/mL inactivated various plant pathogens, including *Erwinia amylovora*, *Xanthomonas arboricola* pv. *juglandis*, *Pseudomonas syringae* pv. *tomato*, and *Allorhizobium vitis*, both in vitro and in vivo.¹²¹ Application of TiO₂-NPs in spinach and maize increased photosynthesis at 0.03%,^{122,123} and at 60 ppm, enhanced the germination of fennel (*Foeniculum vulgare* Mill).¹²⁴ Similarly, at 750 mg kg⁻¹, TiO₂-NPs improved phosphorus content and enhanced metabolite accumulation in rice.¹²⁵ While TiO₂-NPs offer numerous benefits, they can pose potential risks, particularly in relation to ROS generation. At high concentrations, the photocatalytic activity of TiO₂-NPs can result in the overproduction of ROS, leading to oxidative damage in plant tissues. This can impair photosynthesis, cause membrane lipid peroxidation, and lead to chlorophyll degradation. In the soil, TiO₂-NPs may also have negative effects on soil microorganisms, especially those involved in nutrient cycling and decomposition. There is evidence that excessive TiO₂-NP accumulation in the soil could alter microbial community structure, potentially reducing the activity of beneficial microbes such as mycorrhizal fungi and rhizobacteria

Cerium oxide nanoparticles (CeO-NPs)

Cerium (Ce) is a rare earth element that exhibits unique redox properties, allowing cerium oxide nanoparticles (CeO₂-NPs) to act as antioxidants by alternating between the Ce³⁺ and Ce⁴⁺ oxidation states. This redox cycling enables CeO₂-NPs to scavenge ROS, protecting plant cells from oxidative stress. CeO₂-NPs can store and release oxygen depending on the plant's needs, making them highly effective in stress mitigation. CeO₂-NPs are capable of penetrating plant cells and localizing in cellular compartments such as chloroplasts and mitochondria, where they interact with ROS generated during metabolic processes. This ability to scavenge ROS helps plants maintain redox homeostasis, particularly under abiotic stress conditions such as drought and heavy metal exposure. Its high reactivity and inherent antioxidative potential render it capable of scavenging reactive oxygen species (ROS), molecules detrimental to plants especially during stress periods, thereby safeguarding plant cells against damage at the cellular and biomolecular level. This property underscores its potential in enhancing overall plant health and resilience.^{126,127,128,129,130} Evidence from a number of studies underscores the positive impact of cerium on plant growth and development. For instance, Morales et al. (2013)¹³⁰ demonstrated that Cilantro (*Coriandrum sativum*) exposed to CeO-NPs in soil at a concentration of 125 mg/kg exhibited increased root and shoot length. At this concentration, catalase activity significantly increased in shoots, while ascorbate peroxidase activity increased in roots, helping to protect cells from oxidative damage. Similarly, 500 mg/kg nanoceria soil amended enhanced wheat growth (9%), biomass (12.7), and grain yield (36.6%).¹³¹ In alfalfa and cucumber, cerium at 500 mg/L⁻¹ enhanced shoot and root growth in germination experiments.¹³² A notable study conducted by Mohammadi et al (2021).¹²¹ investigated the interaction effects of CeO NPs at concentrations of 25, 50, and 100 mg L⁻¹ foliar spray, along with salinity stress levels of 50 and 100 mM NaCl, on Moldavian balm (*Dracocephalum moldavica* L.). Salinity stress notably decreased agronomic traits, such as leaf and shoot fresh and dry weight,

photosynthetic pigment content, and SPAD, while increasing MDA, H_2O_2 , proline (Pro) content, electrolyte leakage (EL), and antioxidant enzymatic activities (SOD, APX, and GP). However, CeO-NP treatments enhanced the growth performance of plants under salinity stress conditions by improving agronomic traits, photosynthetic pigment content, SPAD, Pro, and antioxidant enzymes. Furthermore, CeO-NPs led to a reduction in MDA, H_2O_2 , and EL through increased antioxidant enzymatic activity under salinity conditions. Among the tested CeO-NP concentrations, 50 mg L^{-1} yielded the most favourable outcomes under both non-stress and salt-stress conditions. The potential mechanism for alleviating salinity stress with CeO-NP involves an increase in low-molecular-weight and water-soluble substances, commonly referred to as osmolytes (e.g., sugar, polyamines, proline). This is a general strategy adopted by plants to cope with salinity stress, as outlined by Sharma et al. (2012).¹³³ In a study by Gui et al. (2015)¹³⁴ involving butterhead lettuce, seeds were grown in potting soil with varying concentrations of CeO_2 nanoparticles (NPs) for 30 days. Results showed that lettuce treated with $100 \text{ mg} \cdot \text{kg}^{-1}$ of CeO-NPs exhibited accelerated growth, albeit with increased nitrate content. Lower concentrations had no notable effect on growth compared to the control, while higher concentrations inhibited growth and biomass production. Besides that, high concentrations disrupted the stress response in lettuce plants, as evidenced by changes in Superoxide dismutase (SOD), Peroxidase (POD), and Malondialdehyde (MDA) activity. These findings highlight the potential benefits of nanoscale cerium, despite its non-essential status for plant growth, when applied at appropriate concentrations.

The precise mechanism underlying the action of cerium oxide nanoparticles (CeO-NPs) remains elusive, necessitating further research. However, some literature suggests that they possess distinctive redox properties, allowing them to transition between +3 and +4 oxidation states similar to cellular antioxidants. In their +4 state, CeO-NPs effectively scavenge free radicals, which are harmful molecules produced during stress conditions, thereby protecting

plant cells. In addition, CeO-NPs have been reported to exhibit enzyme-mimicking capabilities resembling superoxide dismutase (SOD) and catalase, thus enhancing the plant's natural antioxidant defence mechanisms by facilitating the breakdown of free radicals. Furthermore, studies suggest that CeO-NPs may influence plant hormone production or signalling pathways, potentially bolstering stress tolerance and promoting growth. However, the specific mechanisms involved require further investigation.

Silicon dioxide nanoparticles (SiO₂-NPs)

Silica, or silicon dioxide (SiO₂) is widely present in the environment as sand, quartz, and flint. Silica is a key element in agriculture and plant biology, contributing significant benefits to plant growth and health, though not essential for all plants.¹³⁵ In plants, silica deposits in tissues such as the cell wall, where it provides structural strength to support upright growth and, for crops such as rice and wheat, to resist lodging.¹³⁶ Notably, silica boosts plants' resistance to fungal and bacterial diseases by reinforcing plant tissues, making them less penetrable by pathogens.^{136,137} A high silica content in plants can deter pests, making the tissues less appealing or harder to digest,¹³⁸ and it also plays a vital role in enhancing drought resistance by maintaining cell turgidity and reducing water loss.¹³⁹ Beyond being a physical strengthener, silica modulates the availability and uptake of essential nutrients such as phosphorus, potassium, and nitrogen, and helps mitigate the negative effects of toxic metals in plants when grown in contaminated soils.¹⁴⁰ Additional studies also suggest benefits to photosynthetic efficiency.¹³⁸ In agriculture, silica is often added to soil as silicate slags, diatomaceous earth, or certain Si-rich fertilizers. It can also be used in liquid form as a foliar spray, providing a direct supply of silicon to the plant shoots.¹³⁶ Silica naturally exists in soil and is absorbed by plants during nutrient uptake, although its availability depends greatly on factors such as soil pH and type.¹³⁶ While beneficial, balanced use is key, as excessive silica

can disrupt soil chemistry and negatively impact plant growth.^{138,141} The silicon transporter proteins, such as Lsi1, Lsi2, and Lsi6, play a crucial role in transporting SiO₂ from roots to shoots. Specifically, Lsi1 facilitates SiO₂ entry into roots, and while SiO₂ concentration does not affect Lsi1 expression, SiO₂ have been shown to increase the expression of silicon transporter genes like Lsi1 and Lsi2 under salt stress. Additionally, OsLsi1, a silicon-transporting aquaporin (AQP), is upregulated by silicon supplementation, linking silicon to molecular signaling.¹⁴²

Several studies have highlighted the effectiveness of silica nanoparticles (SiO₂-NPs) at various concentrations in enhancing seed germination and plant health. For instance, when tomato seeds were treated with SiO₂-NPs at a concentration of 8 g/L, there were improvements in percent seed germination, mean germination time, seed germination index, seed vigor index, as well as seedling fresh weight and dry weight.¹⁴³ Similarly, SiO₂-NPs at 100 µg/ml was effective in combating the fungal pathogen *Rhizoctonia solani* in wheat. Besides that, these nanoparticles have been shown to mitigate stress in wheat caused by chromium (Cr) contamination in soil, particularly when applied at a concentration of 250 mg/kg⁻¹ soil.^{144–146} These instances emphasize the potential of SiO₂-NPs in agricultural contexts, emphasizing the significance of dosage in attaining desired results. Despite significant research on the benefits of silica in agriculture, there are still significant gaps in our understanding of its precise mechanisms of action, especially at the molecular level. Further research is necessary regarding the specific pathways through which silica enhances plant growth, bolsters disease resistance, and regulates nutrient uptake. Furthermore, uncertainties remain regarding the long-term effects of silica nanoparticles on soil health and ecosystem dynamics.

Table 1: Comparative analysis of metal types in nanofertilizers. This table presents a comprehensive comparison of different metal types used in nanofertilizers, highlighting their primary advantages and potential drawbacks. The analysis provides insights into the benefits each metal type brings to sustainable agriculture and the associated risks that must be managed to optimize their use.

Metal Type	Advantages	Potential Drawbacks
Zinc Oxide (ZnO)	Enhances enzyme activity, improves growth and yield, increases stress tolerance, effective against pathogens.	Potential phytotoxicity at high concentrations, risk of zinc accumulation in soil affecting microbial health.
Copper Oxide (CuO)	Enhances photosynthesis, nutrient uptake, and resistance to ROS, effective against bacterial and fungal pathogens.	Phytotoxicity at high doses, potential for copper accumulation leading to soil and water contamination.
Iron Oxide (FeO)	Essential for chlorophyll synthesis, improves photosynthesis and nitrogen metabolism, enhances soil health.	Risk of iron accumulation in soil, potential oxidative stress to plants at high concentrations.
Magnesium Oxide (MgO)	Improves chlorophyll content, enzyme activation, enhances soil structure, effective against pathogens.	Limited studies on long-term effects, potential for magnesium leaching in sandy soils.
Manganese Oxide (MnO)	Crucial for photosynthesis, nitrogen assimilation, ROS protection, hormone signaling.	Potential phytotoxicity at high concentrations, need for careful management to avoid excess application.
Nickel Oxide (NiO)	Enhances nitrogen metabolism, improves chlorophyll content, stress response activation.	Toxicity at high concentrations, potential negative impact on soil microbes and plant nutrient uptake.
Calcium Oxide (CaO)	Strengthens cell walls, enzyme activation, signal transduction, stress response.	Risk of calcium accumulation affecting soil pH and nutrient balance.
Titanium Dioxide (TiO ₂)	Enhances photosynthesis, nutrient absorption, protection against UV radiation, antimicrobial properties.	Concerns over long-term environmental impact, potential for nanoparticle accumulation in soil and water.
Cerium Oxide (CeO ₂)	High antioxidative potential, enhances overall plant health and resilience, stress tolerance.	Limited understanding of mechanisms, potential environmental and health risks with long-term exposure.
Silicon Dioxide (SiO ₂)	Improves structural strength, disease resistance, drought tolerance, nutrient uptake	Excessive silica can disrupt soil chemistry, limited understanding of long-term

modulation.

effects on plant systems.

The effects of nanometal oxides (ZnO, CuO, FeO, MgO, TiO, CeO, and SiO) on crop improvement are presented in Table 2.

Name of Nanometal oxides	Particle size	Plant tested	Concentration	Productivity	Cited references
ZnO	25 nm	Peanuts	1000 ppm	Enhanced seed growth, stem, and root growth	147
ZnO	175 nm	Strawberry	5x10 ⁻³ M	Effective against the fungal pathogen <i>Botrytis cinerea</i> .	44
ZnO	15 nm	Lettuce	478 µg/mL	Effective against <i>Botrytis cinerea</i> and <i>Sclerotinia sclerotium</i>	48
ZnO	30 nm	Maize	10–25 mM	Effective against <i>Fusarium proliferatum</i> in maize grain storage and during growth	49
ZnO and TiO	20–200 nm	Sweet potato	50 µg/mL	Antibacterial activities against <i>Dickeya dadantii</i> , causing sweet potato stem and root rot disease in China	42,55
ZnO	48.2 nm	Rice	16.0 µg/mL	Effective against <i>Xanthomonas oryzae</i> pv. <i>oryzae</i> (Xoo) strain GZ 0003 causing bacterial leaf blight	55
ZnO	22 nm	Wheat and maize	100 mg/L	Increases the plant growth and grain production	29
ZnO	30 nm	rice	100 mg/L	Protects from chilling stress by enhancing chill related transcription factors and improving anti-oxidant activity	148
ZnO	24 nm	Wheat	500 mg/L	Increases plant growth and grain production	149
ZnO		Cucumber	100 mg/L	Enhances the drought stress tolerance	50
ZnO	60-90 nm	Tomato	25 and 50 mg/L	Enhances drought stress response	30
ZnO	36 nm	Wheat	5 mg/kg	Enhances the crop	46

				production by increasing grain content	
ZnO	97.3 nm	Grapes	25 ppm	Enhances the quality of Crimson seedless (<i>Vitis vinifera</i> L.) table grape berries	47
ZnO	8.9 to 32.6 nm	Tomato	18.0 µg/mL	Effective against <i>Ralstonia solanacearum</i> , causing bacterial wilt disease in tomato	150
ZnO	31.4 nm	Rice	40 ppm	Enhances grain yield	151
ZnO		Tomato	100 mg/L	Effective against the Tomato mosaic virus (ToMV)	152
ZnO	28 nm	Rice	100 mg/L	Improves early growth in rice under cadmium stress	153
ZnO		Eggplant	50 or 100 ppm	Enhances drought stress tolerance	51
ZnO		Tomato	50 ppm	Enhances salt tolerance	52
ZnO	50 nm	Spinach	1000 ppm	Increases protein and dietary fibre	154
ZnO	74.68 nm	<i>Mentha spicata</i> L.	100 µg/mL	Effective against Tobacco mosaic virus in <i>Mentha spicata</i> L.	155
ZnO, MgO and MnO2	56.1–110.0 nm, 10.1–18.8 nm, and 19.8–63.9 nm	Rice	16.0 µg/ml	Effective against <i>Xanthomonas oryzae</i> pv. <i>Oryzae</i>	55,56
ZnO		Rice	50 mg/L	Enhances crop productivity and reduces cadmium toxicity	52
ZnO and CuO	18 nm and 16.8 nm	Citrus	80 mg/ml	Effective against Citrus black rot disease caused by <i>Alternaria citri</i>	156
CuO	50 nm	Bean	500 mg/kg	Increases uptake of soluble Cu, enhancing growth	157
CuO	20-39 nm	Tomato	500 mg/ kg	Increases beneficial bacteria against <i>Ralstonia solanacearum</i> causing tomato bacterial wilt (TBW)	158
CuO		Green onion	150 mg/kg	Enhances allicin content and nutrients	159
CuO	30 nm	Cotton	10 mg/L	Low concentration	69

				enhances the Bt toxin protein production in the leaves and roots of Bt Cotton	
CuO	9.70 nm	In vitro	250 µg/ml	Effective against <i>F. oxysporum</i> and <i>R. solanacearum</i>	160
CuO	75 nm	Lettuce	20 mg/plant	Enhances mineral element uptake	161
CuO		Mustard (<i>Brassica juncea</i>)	4 ppm	Increases photosynthesis and antioxidants level	162
FeO	20-30 nm	Rice	50mg/L	Increases iron uptake and helps in oxidative stress	163
FeO		Wheat and curcumin	0.6 mM and 1.2 mM	Enhances drought tolerance	164
FeO		Ajwain (herb)	100 mg/ L	Enhance the growth in arsenic toxic soil when combined with <i>Providencia vermicola</i> .	165
FeO	20 nm	Peanut (<i>Arachis hypogaea</i>)	1000 mg/ kg	Increases dry biomass and chlorophyll content	79
FeO		Soybean	0.75 g/ L	Increases the grain quality	166
Gamma FeO		Glycine max	500 mg/L	Promotes root elongation	167
MgO	15 nm	Rice	203, 215 and 230 µg/mL,	Effective against <i>Fusarium verticillioides</i> , <i>Bipolaris oryzae</i> , and <i>Fusarium fujikuroi</i>	87
MgO	5-15 nm	Tomato		Effective against fungal pathogens in leaf phyllosphere	88
MgO	100 nm	Tomato	0.05-0.1%	Effective against bacterial wilt caused by <i>Ralstonia solanacearum</i>	90
MgO	100 nm	Tobacco	500 µg/ml	Effective against soil borne pathogen <i>Thielaviopsis basicola</i> and <i>Phytophthora nicotianae</i>	91
Biochar-based MgO		Soil		Increases C-cycling beneficial bacteria in soil	89
TiO₂ (Ag doped)		Potato	0.43 mg/plate	Effective against <i>Fusarium solani</i> causing	118

hollow TiO₂)				Fusarium wilt disease in potato, tomato	
Titanium dioxide nanostructure (TDNS)	3-5µm	Faba Bean	150µM	Control Broad bean stain virus (BBSV) in Faba bean	119
TiO₂	6-8nm	Wheat	0.10mg/ml	Effective against wheat rust (<i>Ustilago tritici</i>)	120
TiO NPs	10-80nm	Tomato	0.5 mg/mL	Involves inactivation of various plant pathogens: <i>Erwinia amylovora</i> , <i>Xanthomonas arboricola</i> pv. <i>juglandis</i> , <i>Pseudomonas syringae</i> pv. and <i>Allorhizobium vitis</i>	121
TiO		Spinach (<i>Spinacia oleracea</i>)	0.03%	Increases the photosynthesis reaction	122
TiO	21nm	Fennel	60 ppm	Increases the seed germination	168
TiO		Maize	0.03%	Increases the chlorophyll content thus enhances the yield	123
TiO	20 nm	Rice	750 mg/ kg	Increases phosphorus and enhances metabolite accumulation	125
Cerium oxide (CeO₂ NPs)	8 nm	Coriander (<i>Coriandrum sativum</i>)	125 mg/kg	Increases root and shoot length	130
CeO₂	23 nm	wheat	500mg/kg	Increases growth, biomass and grain yield	131
CeO	42 nm	Barley (<i>Hordeum vulgare</i>)	500 - 1000 mg/kg	Affects growth, biomass and grain yield	169
CeO	7 nm	Alfalfa, cucumber	500 mg/L	Enhances shoot elongation	132
SiO	12 nm	Tomato	8 g/L	Increases seed germination and biomass	143
SiO	9.92 nm and 19.8 nm	wheat	100 µg/ml	Effective against <i>Rhizoctonia solani</i>	145
SiO	15-24 nm	Wheat	250 mg/ kg	Reduces the effect of chromium (Cr) in Cr contaminated soil	144
SiO		Carrot (<i>Daucus carota</i>)	0.05 and 0.10 mg/ ml	Used in disease management; affects nematode <i>Meloidogyne</i>	170

L.)*incognita*

Potential Risks and Risk Management Strategies for NMOFs

Use of synthetic chemical fertilizers and pesticides in agriculture carries inherent risks, which are amplified by their excessive use. The overapplication of these chemicals can lead to a range of environmental and health issues, underscoring the need for cautious management of agrochemicals. These concerns similarly apply to nanometal oxide fertilizers (NMOFs), and other metallic nanoparticles employed in agriculture, particularly given the notable deficiency in comprehensive soil and field research in this domain. Although these advanced materials offer substantial advantages, they also introduce potential risks, closely tied to their unique nanoscale properties, and these risks must be both recognized and managed. The micronutrient market represents a significant sector within the agricultural industry, generating substantial revenue. In fact, the global market size projection for agricultural micronutrients is at \$7.78 billion by 2030, up from the current \$4.87 billion in 2023.¹⁷¹ Nonetheless, it is important to acknowledge that excessive concentrations of trace elements can have detrimental effects on plants and impact the quality of food for human consumption. Metal toxicity in humans is a significant hazard, often stemming from the consumption of contaminated foods. Hence, careful administration of NMOFs use and diligent monitoring of trace element levels in agricultural practices are imperative in order to safeguard both environmental and human health, as well as to maximize benefits of their use.¹¹ The literature is replete with studies demonstrating that the application of nanomaterials on crops at elevated levels can lead to adverse effects on plants, including inhibited growth, failed and reduced germination, pigment depletion, and compromised yields.^{69,31,53,67,107,172} As discussed further below, the detrimental impacts of NMOs on plants depends greatly on factors such as particle size and shape, concentration, composition, aggregation, exposure duration, method

of application, environmental factors, plant species, and growth stage [Illustrated in **Figure 1**].^{69,31,53,67,107,172,173} In addition, the method of applying these materials plays a crucial role in determining the level of risk they pose. If not used appropriately and judiciously, the accumulation of nanomaterial oxides (NMOs) in the environment and the food chain could pose substantial risks to non-target systems, including various plants, pollinators, soil microorganisms, aquatic ecosystems, terrestrial animals, and humans (illustrated in **Fig. 2**).^{174–177} In **Fig. 2**, we present a graphical representation of the potential toxicity effects of NMOs on different forms of life. This data was derived from the limited available literature and further enhanced using an AI model to generate an interactive graph. ZnO, SiO₂, and iron oxides are abundant materials widely used in various applications, from domestic products to agriculture, and are consequently released into different environments.¹⁷⁸ Reports indicate that 60-90% of these nanomaterials end up in landfills, with 10-25% being disposed of in water systems.¹⁷⁹ Soil application and leaching significantly contribute to increased toxicity levels, which can be mitigated through several strategies. The high solubility of nanomaterials is also a critical factor for higher leaching levels. Encapsulating nanofertilizers in less soluble coatings can provide a slow-release mechanism, reducing their immediate impact. Predicting the leaching of nanomaterials in soil and water involves a combination of experimental studies (e.g., soil column and batch experiments), modelling approaches (e.g., HYDRUS¹⁸⁰ and COMSOL¹⁸¹), and understanding the physicochemical properties of the nanomaterials. By refining these models, incorporating controlled-release formulations, optimizing application rates, and monitoring environmental impact, we can significantly reduce the potential toxicity of NMOs. Nonetheless, there remain a number of unanswered questions regarding the potential toxicity of NMOs to humans through agricultural products and practices. The utilization of NMOs can have implications for soil health by affecting soil microorganisms, modifying soil chemistry, influencing nutrient availability, and impacting

the biodiversity of both soil and water ecosystems.^{172,182–184} Understanding how to manage the delicate balance between reaping the intended agricultural benefits and mitigating potential risks stands will be critical to integrating these advanced materials into food production practices.

Currently, there is limited mention of existing or proposed regulatory frameworks specifically designed to monitor and control the application of NMOFs in agriculture. However, as the use of nanomaterials in farming increases, it becomes essential to develop clear policies, regulations, and standards to govern their use, mitigate risks, and protect both environmental and human health. A comprehensive regulatory framework for nanometal oxide fertilizers (NMOFs) should address several critical aspects to ensure their safe and effective use. First, regulatory bodies need to establish safety thresholds that define safe exposure limits for different types of NMOFs, considering both short- and long-term impacts on soil, plants, water systems, and human health. Additionally, environmental impact assessments (EIAs) should be mandated before large-scale application of NMOFs, evaluating their effects on soil health, water quality, biodiversity, and non-target organisms such as pollinators and soil microorganisms. Human health standards must also be implemented, specifying acceptable limits for trace metal concentrations in crops to prevent metal toxicity, with labeling and traceability requirements ensuring transparency in NMOF-treated food products. A regulatory framework should include monitoring and reporting mechanisms to track the environmental and health impacts of NMOF applications, possibly through national or regional databases. Furthermore, industry guidelines and best practices should be developed in collaboration with regulatory bodies to recommend application rates, methodologies, and risk mitigation strategies, ensuring safe usage. Lastly, international collaboration is essential for harmonizing guidelines across countries to prevent cross-border risks and maintain uniform safety standards in agricultural practices involving NMOFs.

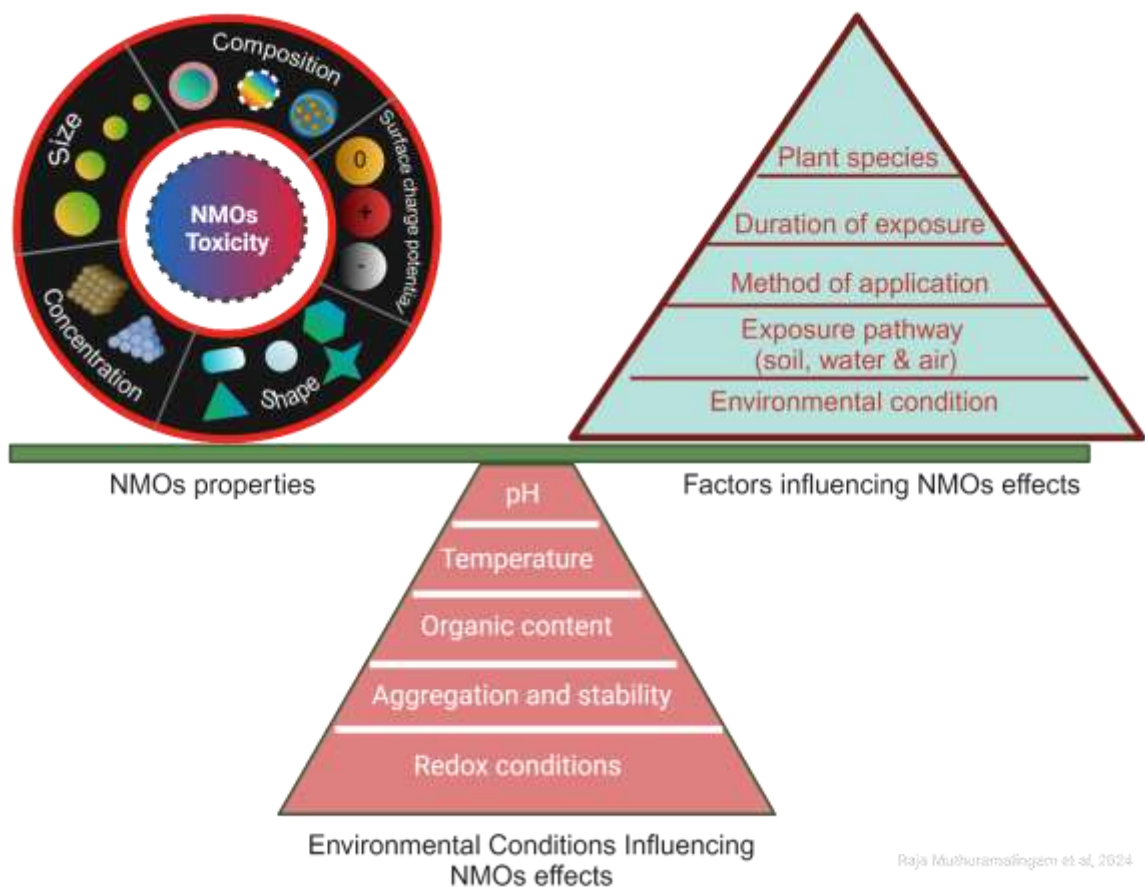


Figure 1. Schematic representation of the multifactorial influences on the toxicity of nanometal oxides (NMOs). The left panel depicts the intrinsic properties of NMOs, including size, shape, concentration, composition, and surface charge potential, which are fundamental in determining their toxicity. The right panel outlines key extrinsic factors such as plant species, duration of exposure, method of application, exposure pathways (soil, water, and air), and environmental conditions that interact with NMOs' properties to shape their environmental and biological effects. The lower section emphasizes the importance of environmental conditions like pH, temperature, organic content, aggregation stability, and redox conditions in modulating the impact of NMOs. Understanding and balancing these parameters is critical for assessing the ecological and health risks associated with NMOs in agricultural and environmental contexts.

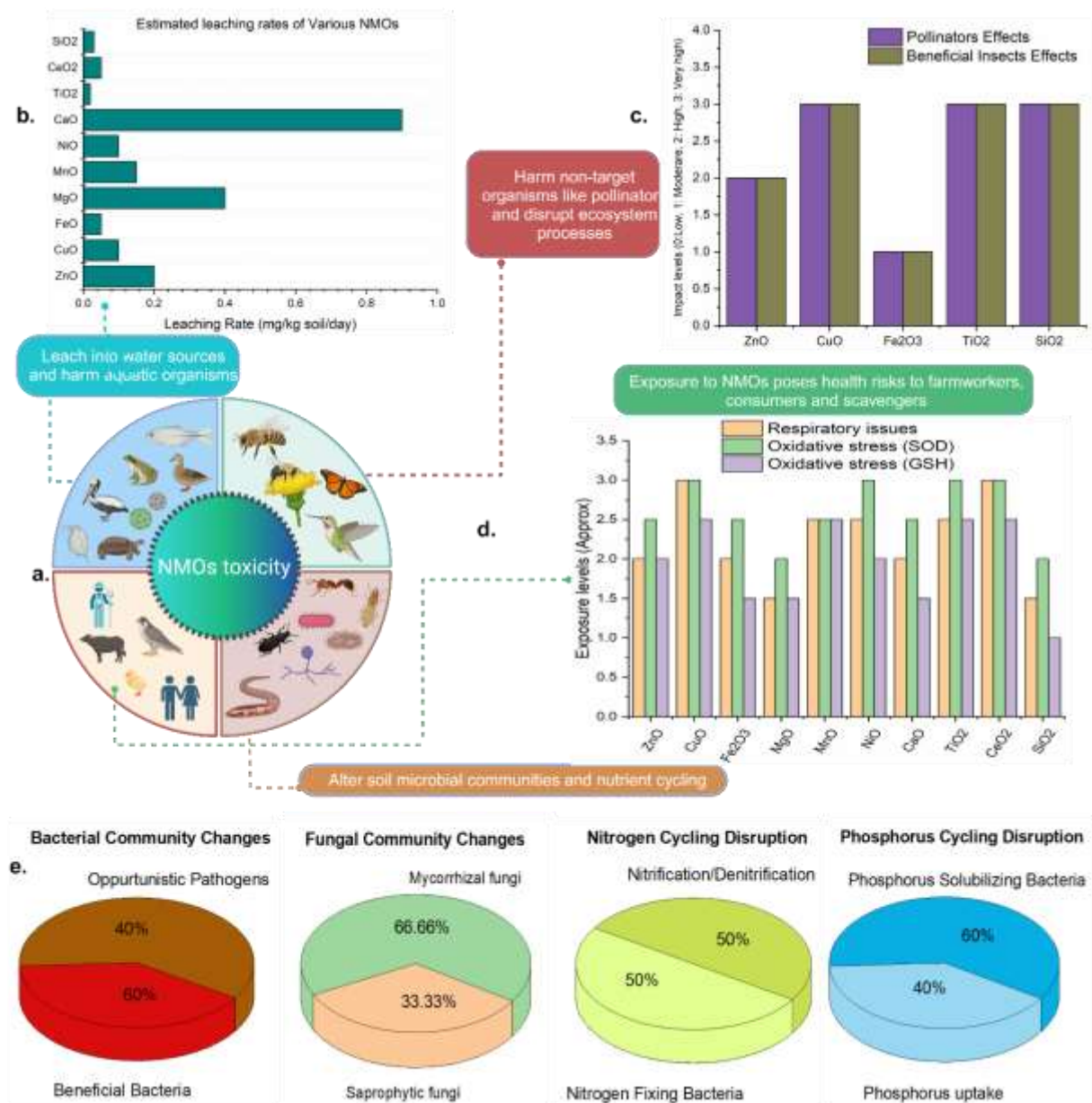


Figure 2. Illustrates the potential harmful effects of nanometal oxides (NMOs) on various forms of life. The accumulation of NMOs in ecosystems and the food chain poses significant risks to unintended organisms, including pollinators, soil microorganisms, aquatic life¹⁷⁹, terrestrial plants, animals, and humans. Many aspects of these interactions remain poorly understood and require further study. a. NMOs Toxicity: Representation of different environmental compartments affected by NMOs, with hypothetical quantitative data points from the limited available literature. b. Estimated Leaching Rates of Various Nanofertilizers: This graph illustrates the estimated leaching rates (in mg/kg soil/day) of different nanofertilizers in soil.^{185,186} The leaching rates reflect the mobility of these nanomaterials in the soil and their potential environmental impact. c. Bar chart showing the impact on pollinators and beneficial insects by different nanoparticles (ZnO, CuO, Fe₂O₃(FeO), TiO₂, SiO₂) across various impact levels. d. Bar chart depicting exposure levels of NMOs and associated health outcomes, such as respiratory issues, oxidative stress (SOD), and oxidative stress (GSH).¹⁸⁷ e. Pie charts illustrating changes in bacterial community (beneficial bacteria vs. opportunistic pathogens), fungal community (mycorrhizal fungi vs. saprophytic fungi),

nitrogen cycling disruption (nitrogen-fixing bacteria vs. nitrification/denitrification), and phosphorus cycling disruption (phosphorus-solubilizing bacteria vs. phosphorus uptake).

Role of NMOF Concentration

The multifaceted nature of nanometal oxide fertilizers (NMOFs) in agriculture encompasses not only their chemical attributes but also the critical aspects of concentration and timing of their application.¹⁸⁸ Nanotechnology's role in agriculture surpasses simple nutrient provision, enabling precision in the chemical engineering of fertilizers for controlled, dissolution, and environmentally responsive release, thus ensuring nutrients are delivered at the optimum time and in appropriate quantities. This controlled release technology significantly boosts efficiency and reduces waste, while the ability to respond to environmental cues like soil moisture, pH, or temperature variations optimizes plant growth and minimizes nutrient leaching. However, the effectiveness and safety of NMOFs hinge on their concentration; overly high concentrations may harm plant and soil health by causing phytotoxicity or disturbing soil microbial communities.¹⁸⁹ Identifying the ideal concentration for agricultural purposes is therefore essential for balancing effectiveness and environmental stewardship. Different crops exhibit distinct nutrient requirements and reactions to NMOFs. It is, thus, essential to consider these plant-specific needs to ensure that the concentration of the fertilizer aligns with the temporal requirements of each crop. The distinct impacts of various nanoparticle types, such as zinc oxide or copper oxide, on plant development necessitate tailored concentration levels to fully leverage their advantages while safeguarding plant health and the environment. Besides, the potential effects of NMOFs on non-target organisms, like beneficial soil microbes and pollinators, demand careful consideration. Employing these fertilizers in lower concentrations is advised to mitigate environmental risks and preserve ecological balance, thereby ensuring biodiversity and the sustainability of agricultural practices.

Role of NMOF Composition

The composition of NMOFs plays a crucial role in determining their reactivity and potential toxicity, with various factors influencing their properties.¹⁹⁰ NMOFs typically consist of primary active ingredients, such as simple or complex metal precursors, alongside secondary components like carrier mediums, stabilizers, dispersants, nutrients, coatings, and targeted delivery additives. While NMOFs formulated with biologically derived secondary ingredients often present lower risks, those containing chemically toxic components may pose greater hazards. Therefore, ensuring a well-balanced formulation where primary active ingredients are effectively complemented by secondary components is essential for managing risks associated with NMOFs. In managing these risks, strategies should prioritize the use of biologically derived secondary components whenever feasible, as this can help reduce overall toxicity. One effective approach to mitigate toxicity related to NMOF composition is adopting biological and green synthesis methods.^{25,191} Unlike traditional chemical synthesis, which relies on toxic solvents, catalysts, and reagents, biological and green synthesis methods utilize naturally occurring biological agents like enzymes or microorganisms.^{192,193} By leveraging these agents, the synthesis process can occur without the need for harmful chemicals, aligning with principles of sustainability and environmental responsibility. Furthermore, utilizing waste stream biomass for synthesizing nanocarriers presents a promising avenue towards a circular economy while reducing costs. Examples include the production of nanocellulose or nanolignin from wood waste.¹⁹⁴ This approach not only minimizes the risk of toxicity associated with NMOF composition but also decreases the likelihood of adverse interactions with biological systems. By repurposing waste materials into valuable nanocarriers, this strategy contributes to both environmental sustainability and economic efficiency.^{195,196}

The Role of NMOF Size, Shape, and Surface Charge

Smaller NMOFs (~1-100 nm) have a greater propensity to permeate plant tissues and cell walls.¹⁹⁷ This phenomenon can result in enhanced nutrient uptake and utilization by plants.¹⁷⁶ Nonetheless, the reduced size of NMOFs also engenders concerns regarding potential toxicity. Excessive uptake of nanoparticles can lead to their accumulation within plant tissues, potentially culminating in toxicity. Multiple studies have documented instances of phytotoxic effects, including inhibited growth and cellular damage, attributed to the undue accumulation of nanoparticles.¹⁹⁸ Conversely, larger NMOFs (~100-200 nm) are generally considered to be less toxic due to their diminished capacity for penetration and accumulation within plant tissues.¹⁹⁹ Based on the literature reviewed, multiple studies indicate that NMOFs within the size range of 20-40 nanometres (nm) demonstrate the most effective promotion of plant growth compared to both smaller and larger particles.^{25,191} However, the effectiveness of NMOFs relies heavily on their interaction with typical plant tissue pore sizes. The waxy cuticle, serving as a protective barrier against water loss and pathogens, generally exhibits pore sizes ranging from 0.1 to 10 micrometres (μm), although this can vary depending on plant species, environmental conditions, and developmental stage. Stomata, responsible for gas exchange and water regulation, typically have dimensions varying among plant species, with widths ranging from approximately 3 to 12 micrometres (μm) and lengths from 10 to 40 micrometres (μm). Environmental factors such as light intensity, humidity, and carbon dioxide levels can further influence stomatal size and density.

In addition to size of NMOFs, the geometry or morphology of NMOFs plays a pivotal role in shaping their behaviour and interaction with plants. Distinctive shapes, such as spherical, rod-like, or irregular, can influence how NMOFs are adsorbed on plant tissues, as well as absorbed and distributed within plant tissues.^{200,201} Spherical nanoparticles are frequently favoured for their uniformity and ease of synthesis. Their shape facilitates ready absorption by plant roots and subsequent distribution throughout the plant, subject to size restrictions

noted above.²⁰⁰ On the other hand, rod-shaped or elongated nanoparticles may yield diverse effects on plants contingent on their orientation and interaction with root structures.^{202,203} Borgatta et al. (2018)²⁰⁴ conducted a study investigating the impact of two different morphologies of copper phosphate nanosheets and nanorods. They observed that nanosheets demonstrated greater retention on leaf surfaces compared to nanorods, indicating variation in benefits and toxicity based on morphology. Furthermore, it's crucial to acknowledge the dynamic nature of particle morphology. Processes like dissolution and corona formation can induce changes in shape, although not as prominently as changes in size. Nevertheless, these dynamic alterations can still influence the behaviour and bioavailability of nanoparticles within plant systems. Conversely, the uniformity of NMOFs may offer more consistent and predictable effects on plant growth and nutrient uptake, potentially making them safer and more efficient in agricultural applications.

Plant nutrients, encompassing ions with positive (cations) or negative (anions) charges such as Ca^{2+} , K^{+} , NH_4^{+} , Mg^{2+} , NO_3^{-} , PO_4^{3-} , Cl^{-} , and SO_4^{2-} , are indispensable for supporting plant growth, with many of such nutrients being rapidly absorbed through foliar sprays. However, when considering nanofertilizers like nanometal oxides, the surface charge assumes a pivotal role in their behaviour when applied foliar. Positively charged nanoparticles tend to strongly adhere to negatively charged leaf surfaces, potentially augmenting foliar uptake, albeit excessive positive charge could obstruct stomatal penetration.^{205,206} Conversely, negatively charged nanoparticles exhibit lower adhesion but still gain entry into leaves through passive diffusion or specific transporters.²⁰⁷ Positively charged nanoparticles may induce plant stress responses due to electrostatic interactions with cell membranes, which could impact growth and yield. In contrast, negatively charged nanoparticles generally carry a lower risk of inducing stress but possess the capacity to influence specific metabolic pathways contingent on their composition.^{208,209} The optimization of nanoparticle surface charge facilitates

enhanced adhesion, improves delivery along preferred routes, and minimizes the potential stress responses in plants during foliar applications. For root system, Sun et al. (2019)²⁰⁷ conducted a study focusing on the surface charge's impact on the uptake of approximately 4 nm CeO₂ nanoparticles (NPs) applied to tomato roots hydroponically. Using synchrotron-based X-ray fluorescence microscopy, they analysed the lateral spatial distribution of Ce in tomato leaves. Positively charged CeO₂ NPs showed a stronger association with roots compared to negatively charged NPs, likely due to electrostatic interactions with the negatively charged root surfaces, particularly notable in tomatoes owing to their larger root surface area. Positive NPs tended to remain adhered to roots without transformation, while neutral and negative NPs were more efficiently translocated from roots to shoots. Tomato and lettuce exhibited higher translocation efficiency compared to corn and rice. Positive and neutral treatments led to the formation of Ce clusters outside the main leaf vasculature in the mesophyll, whereas the negative treatment resulted in Ce primarily within the main leaf vasculature across plant species. Notably, in dicot plants, Ce spread further outside the main vasculature compared to monocot plants, likely due to the larger airspace volume in dicot leaves. These findings provide valuable insights into how plant structure and NP surface charge influence metal transport and NP distribution within plants. Therefore, understanding the charges associated with both conventional plant nutrients and nanofertilizers is paramount for refining fertilization practices, ensuring a harmonious supply of cations and anions, and nurturing ideal nutrient uptake to foster robust plant growth.

The Role of Application Method

Proper management of nanofertilizer application is crucial for optimizing their advantages in agriculture while mitigating environmental and human health risks. Nanofertilizers, including NMOFs, must be applied judiciously to deliver the right amount at the right time and in the right place, adhering to the principles of the "3 Rs": meeting plant needs without harming

ecosystems. The choice of application method, such as foliar spraying, seed nanoprimering, or soil amendment, significantly influences their distribution and uptake by plants. Inappropriate application can result in environmental contamination and unintended exposure to non-target organisms. Excessive use of nanofertilizers can lead to nutrient runoff, contributing to water pollution and eutrophication.²¹⁰

To ensure responsible and effective nanofertilizer application, several key strategies can be employed. Firstly, nutrient monitoring involves the regular assessment of plant nutrient levels, enabling the precise determination of nutrient requirements. Nanosensors can be utilized for real-time monitoring of nutrient levels, providing accurate data to adjust nanofertilizer application rates accordingly.²¹¹ This helps prevent the over-application of nanofertilizers, optimizing resource use, and minimizing potential environmental impacts. Secondly, precision application techniques such as controlled-release systems, GPS-guided equipment, and drone technology can be utilized to reduce excess application, ensuring that nutrients are delivered efficiently to plants and maximizing their uptake. Examples of such techniques include fertigation and foliar spraying. Lastly, the implementation of Good Agricultural Practices (GAPs) plays a vital role in minimizing the risk of nutrient runoff and environmental contamination. GAPs encompass a range of measures, including soil testing, nutrient management plans, and runoff prevention measures, collectively working to promote sustainable and responsible nanofertilizer use.²¹²

Nanomaterial Behavior in Different Environmental Conditions

The behavior of nanometal oxide fertilizers (NMOFs) can vary significantly depending on environmental conditions such as pH, temperature, and organic content in soil and water systems. These factors influence the degradation, persistence, mobility, bioavailability, and ultimately, the toxicity of NMOFs in agricultural environments.

pH: Soil pH plays a critical role in determining the solubility and mobility of NMOFs. In acidic soils, certain nanomaterials such as ZnO-NPs and FeO-NPs may dissolve more readily, releasing metal ions at a faster rate. This can enhance their bioavailability but also increase the risk of metal toxicity to plants and soil microorganisms. Conversely, in alkaline soils, NMOFs may remain more stable and persist for longer periods, potentially leading to accumulation and reduced bioavailability.

Temperature: Temperature influences the reaction kinetics of nanomaterials, including their degradation and interaction with other substances in the environment. At higher temperatures, the chemical reactions involving NMOFs, such as oxidation and dissolution, may accelerate, altering their behavior and increasing their mobility in the soil. Warmer conditions can also affect the interaction between NMOFs and organic matter, influencing how these nanoparticles are bound or transported through the soil and water systems.

Organic Content: The organic matter in soil can bind to NMOFs, affecting their mobility and bioavailability. In soils rich in organic matter, NMOFs may form complexes with organic molecules, which can either reduce their movement by binding them to soil particles or enhance their mobility by forming more soluble complexes. This interaction can also alter the toxicity of NMOFs, as the bound forms may have reduced biological activity compared to free nanoparticles. However, in soils with low organic content, NMOFs may remain in their active form, increasing the risk of leaching into water systems and potentially harming aquatic life.

Aggregation and Stability: Environmental factors like ionic strength, salinity, and soil texture can influence the aggregation of NMOFs. In high-salinity environments or soils with fine particles, NMOFs may aggregate more readily, reducing their mobility and bioavailability. However, this can also mean that NMOFs persist longer in these

environments, posing risks of accumulation over time. In contrast, low-salinity environments may lead to greater nanoparticle dispersion, enhancing their mobility but increasing the risk of contaminating groundwater.

Redox Conditions: In anaerobic (low-oxygen) conditions, such as in waterlogged soils, the redox potential of the environment can alter the chemical form of NMOFs, influencing their reactivity and solubility. For example, iron oxides may undergo reduction, changing from Fe^{3+} to Fe^{2+} , which can impact their mobility and interaction with plants. These redox changes can also influence the release of metal ions from nanoparticles, altering their toxicity profile.

Understanding how these environmental factors affect the behavior of NMOFs is crucial for assessing their ecological impact and developing strategies to minimize potential risks. A deeper analysis of these interactions can help optimize the design and application of NMOFs in agriculture, ensuring that they provide the intended benefits while minimizing harm to soil health, water quality, and non-target organisms.

Uptake, Transport, and Metabolism of Nanofertilizers

The processes of uptake, transport, and metabolism of NMOFs in plants are complex, influenced by various factors including the physicochemical properties of the nanoparticles, plant species, growth stage, and environmental conditions.^{213,214} Nanoparticles can be delivered to plants through several pathways like foliar spray, seed coating, soil application, or hydroponic culture.²¹⁵ Nanoparticles applied to leaves are primarily absorbed through either stomatal openings (ranging from 0.866 to 1 mm) or the cuticle via transcuticular pores, a phenomenon that is highly restrictive as a function of pore size (<1 nm). The literature clearly demonstrates that particles smaller than 50 nm can infiltrate through stomata, whereas those with a size smaller than 10 nm can breach the cuticle. The foliar absorption of

nanoparticles is subject to plant species, as it dictates the dimensions and arrangement of stomata and cuticle pores, as well as the physiological processes of the leaf surface (i.e., pH, redox environment, phyllosphere activity), thereby influencing the uptake process. Foliar application of nanofertilizers, along with adjuvants or surfactants, increases retention on the leaf surface or even aids in abrading the cuticle to enable direct uptake by leaves, thus overcoming certain limitations associated with root uptake.^{18,216}

NMOFs can also be absorbed by plant roots through mechanisms that leverage both physical structures and chemical gradients. These gradients might be influenced by rhizosphere chemical conditions such as low pH, organic acids, and other exudates, as well as more active microbiomes.²¹⁷ However, absorption typically starts with passive transport, wherein nanoparticles adhere to root surfaces driven by a concentration gradient and the flow of water in the transpiration stream, akin to nutrient uptake. Root hairs, tiny extensions on the root surface, play a crucial role in this process by significantly increasing the area available for absorption. These hairs create a vast interface between the soil and the root, optimizing the exchange of both nutrients and nanoparticles. In the soil, nutrients, including minerals and ions, are often at higher concentrations than inside the root cells, creating a concentration gradient that naturally drives these substances towards the roots. This process, aided by water flow, reflects how nanoparticles also travel towards the roots. Upon reaching the root surface, nanoparticles may enter the cells via the plasma membrane. This penetration could occur through specialized routes such as ion channels or transporters, which regulate the entry of these particles into the plant's internal system. In the context of seeds, nanoparticles might enter through the micropyle, a tiny opening in the seed coat.²¹⁸ This opening, which naturally facilitates the entry of water and nutrients during germination, could also serve as a gateway for nanoparticles during the seed priming process.

Upon absorption, nanofertilizers are transported within the plant through two primary routes: the apoplastic and symplastic pathways.^{216,219} The apoplastic pathway, which moves along cell walls and intercellular spaces, is generally more conducive for the transport of larger nanoparticles, potentially up to a few hundred nanometers in some cases. In contrast, the symplastic pathway facilitates the movement of smaller particles (10-100 nm) through the cytoplasm of interconnected cells. This intracellular transport is enabled by plasmodesmata, which are microscopic channels linking adjacent cells, and is aided by specific protein transporters. Once nanoparticles have entered the symplastic pathway, they progress cell-to-cell via the plasmodesmata, ultimately reaching the plant's vascular system, the xylem and phloem.²²⁰ The Derjaguin-Landau-Verwey-Overbeek (DLVO) model is often used to study these interactions with the surfaces of the plant vascular system, where electrostatic and van der Waals forces play crucial roles in the adhesion and movement of nanoparticles.²²¹ Once inside the plant, nanoparticles travel through the vascular system, particularly the xylem and phloem, distributing nutrients to various parts. Nanoparticles or their ionic forms are loaded into the xylem vessels and transported upward to the aerial parts of the plant through the transpiration pull. Once in the leaves, they can be redistributed to other parts of the plant via the phloem. Both anions and cations move through the symplastic route, diffusing through the cytoplasm of cells and then through the plasmodesmata, eventually reaching the xylem.

The selective permeability of cell membranes and the lack of a specialized transport system for nanomaterials mean that large and hydrophilic molecules and ions do not easily cross cell membranes.²²¹ However, the electrochemical gradient and membrane potential facilitate the movement of these particles. This mechanism allows nanoparticles, akin to nutrients, to be transported to the shoot system through the xylem vessels to various parts of the plant, ensuring a distribution similar to that of traditional nutrients. Nanoparticles use both passive and active transport mechanisms, which can depend on their size, charge, and the plant's

current needs.²²² Understanding these mechanisms is crucial for developing efficient fertilizers that minimize waste and environmental impact [Refer **Figure 3**].

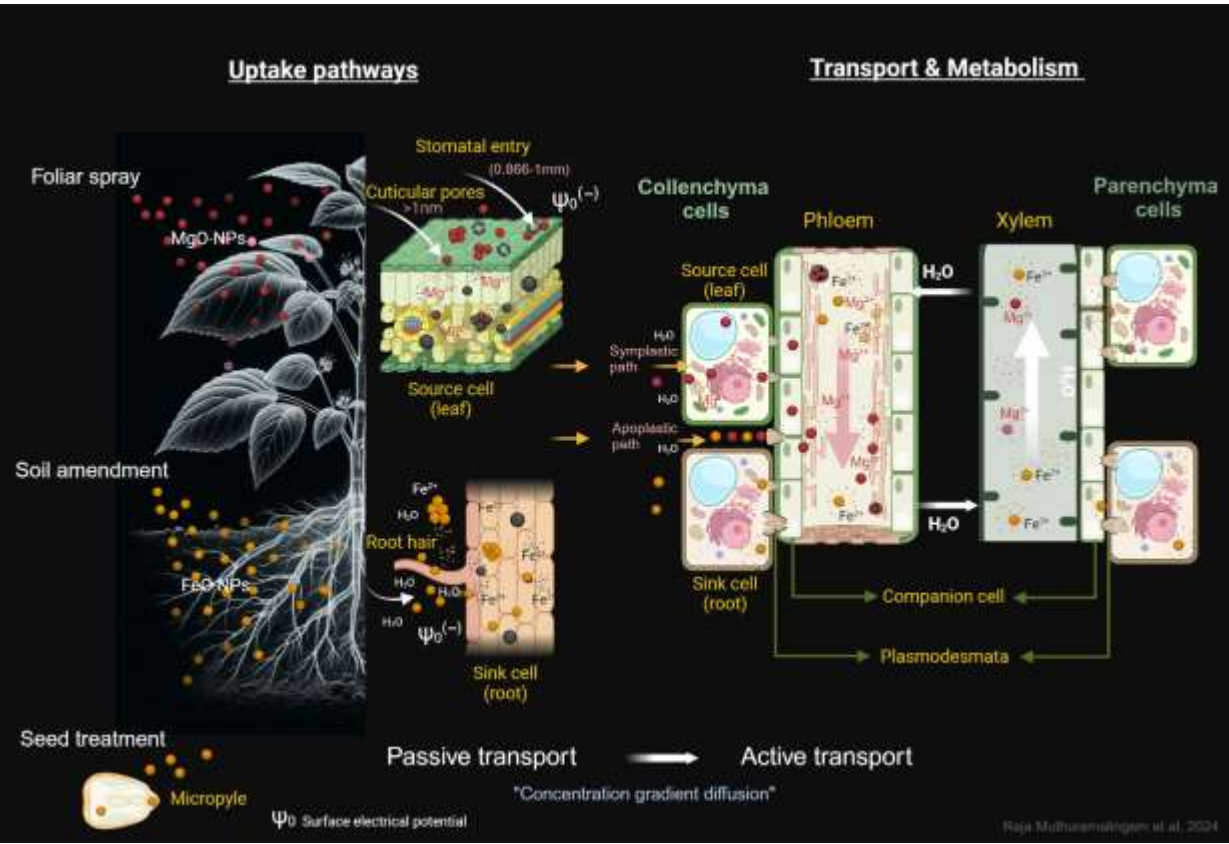


Figure 3. Illustrating the potential routes of uptake for NMOs and their transportation within the plant's physiological system to reach regular nutrient metabolism.

Inside the plant, the metabolism of nanoparticles is dynamic and time-dependent, involving processes such as dissolution, agglomeration, and oxidation. Whether nanoparticles maintain their integrity within the plant depends on their specific type and the in planta environment.^{223,224} These transformations affect their movement within the plant, their potential toxicity, and their availability to the plant's biological systems.²²⁵ Nanoparticles can accumulate in different tissues such as leaves, stems, and roots, with accumulation influenced largely by surface charge potential and, to a lesser extent, by size and tissue conditions. The interaction of these particles with cellular components, including membranes, proteins, and

enzymes, significantly influences their mobility and potential toxicity.^{214,226,227} Moreover, the release rate of nutrients from nanofertilizers is contingent on their composition and coating materials.²²⁸ Physicochemical transformations include dissolution into ionic forms, as seen with zinc oxide nanoparticles (ZnO-NPs) dissolving into zinc ions (Zn^{2+}), essential for physiological functions, and aggregation into larger, less bioavailable particles influenced by internal pH and organic molecules. Chemical transformations involve redox reactions, such as iron oxide nanoparticles (FeO-NPs) being reduced or oxidized, and complexation with organic molecules, altering their bioavailability. Biological interactions can include enzymatic degradation, though specific pathways are not well understood, and sequestration in tissues or cellular compartments to mitigate toxicity, as observed with gold nanoparticles (Au-NPs) accumulating in vacuoles. Studies show that ZnO-NPs dissolve into Zn^{2+} ions, supporting plant growth, FeO-NPs facilitate chlorophyll synthesis, and Cu-NPs, though primarily antimicrobial, can form complexes reducing bioavailability. Once the nanoparticles are assimilated and utilized within the nutrient pathways, excess or unused nanoparticles or their transformed products might be excreted back into the rhizosphere through root exudates. Some nanoparticles or their ions are stored in vacuoles or bound to specific proteins for future use. During senescence or in response to nutrient demand, stored nutrient ions can be remobilized and transported to growing tissues or reproductive organs.

Controlled release of NMOFs

The controlled- or even responsive-release of nanometal oxide fertilizers presents a promising solution, offering precise nutrient delivery, sustained release, and reduced waste, thereby maximizing plant uptake of supplied nutrients.^{229–231} Central to this innovation are nanocarriers, nanostructures designed to encapsulate and deliver nutrients with spatial and temporal precision. These carriers can be tailored from diverse materials, each with distinct

attributes. Biopolymer-based nanocarriers, for instance, offer biodegradability and controlled release through pore structures, while metal-organic frameworks (MOFs) provide high loading capacity and tunable surface chemistry for specific nutrient binding.^{232,233} Nanocarriers form the foundation of controlled-release NMOFs, typically nanoscale materials that encapsulate or transport metal oxide fertilizers. Their controlled-release properties lend themselves to gradual discharge of encapsulated nutrients over time, safeguarding against rapid leaching and degradation. The rate of this release can be tuned by controlling the chemistry of the carrier. Examples encompass nanoparticles, nanocomposites, and nanogels.^{232,233} Polymers like polylactic acid (PLA) are biodegradable green plastics that degrade in response to soil conditions such as temperature (typically below 30°C), moisture, pH, aeration, and microbial action. During degradation, PLA releases nutrients gradually into the soil, contributing to fertility.²³⁴ Biopolymers like chitosan, environmentally friendly and tunable, can target specific soil pH or microbial activity for triggered release [Illustrated in **Figure 4**].^{235,236} Sustained release is integral to preventing nutrient loss from leaching and runoff.²³⁷ This is achieved through gradual nanocarrier or coating degradation, facilitating controlled nutrient diffusion into the soil.²³⁸ Alongside sustained release, triggered mechanisms respond to environmental cues, releasing nutrients precisely when and where needed, optimizing utilization and minimizing waste.^{229,239} Controlled-release NMOFs offer myriad benefits, including reduced runoff for water quality protection, enhanced nutrient efficiency, minimized fertilizer application, and targeted delivery to specific plant tissues.

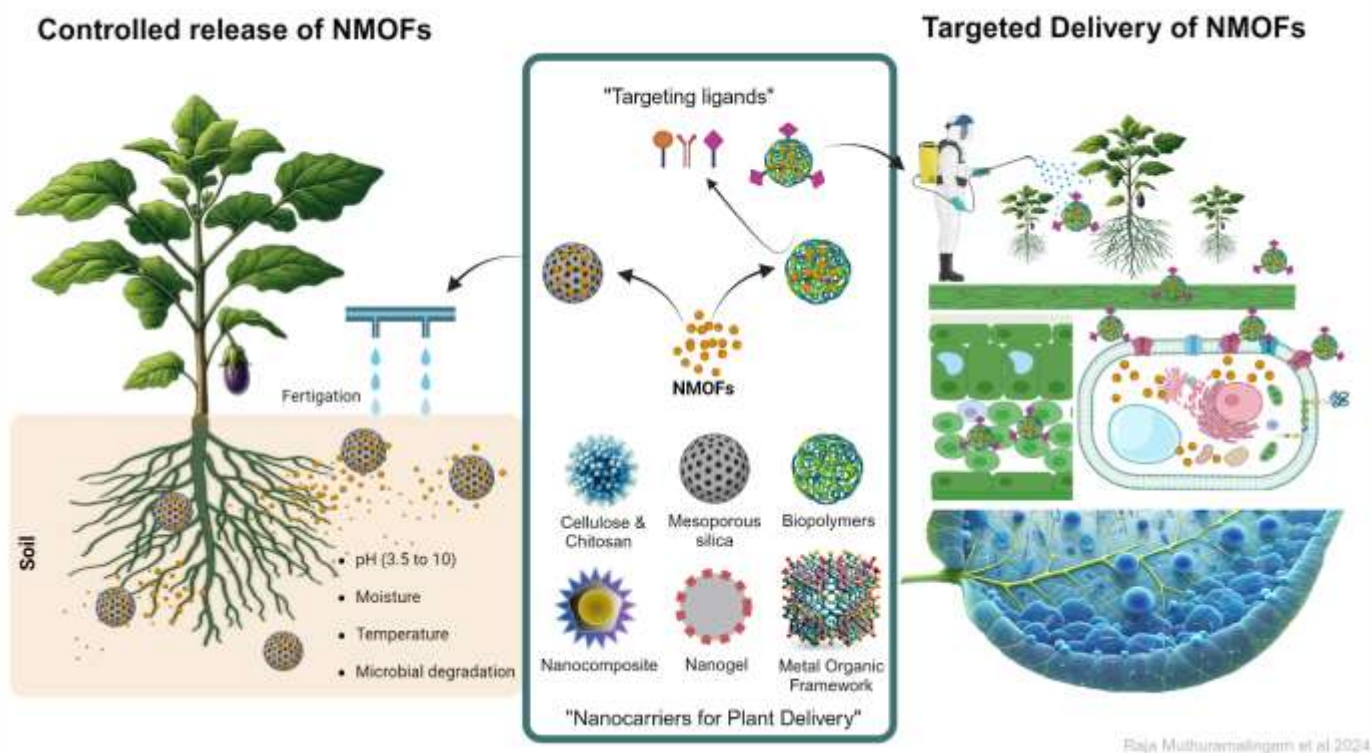


Figure 4. Advancements in agriculture: Illustrating the sophisticated process of controlled release and targeted delivery of NMOFs to enhance plant growth and health.

Targeted release of NMOFs

In contrast to controlled release, targeted release represents a highly precise approach that expands upon the concept of controlled release by incorporating spatially specialized targeting features. While controlled-release nanofertilizers are engineered to regulate the gradual dispersion of nutrients, targeted release integrates specific functionalities that facilitate the direct transportation of nutrients to particular plant cells or tissues or organelles.^{240,241} Here, the delivery vehicle that not only releases its cargo gradually but also navigates with high accuracy to reach its designated destination.²⁴² This novel approach has sparked a number of innovative strategies for delivery. Ligand-Based Targeting (LBT) entails modifying nanofertilizers with ligands, which are molecules capable of selectively binding to plant cell receptors. This modification ensures the exact delivery of nutrients to specific

locations within the plant [Illustrated in **Figure 4**]. Ligands can take the form of antibodies, peptides, or small molecules (hormones), possessing a remarkable affinity for receptors located on the surface of plant cells. Plants are equipped with various receptors that can receive and respond to both internal and external signals, with these receptors playing pivotal roles in processes like nutrient uptake and cellular signalling.^{243,244} The selection of ligands depends on the specific nutrient being targeted and the unique physiology of the plant in question. For example, if the objective is to supply iron to a plant, ligands that bind specifically to iron transporters on root cells may be chosen.²⁴⁵ The ligands attached to the nanofertilizer's surface are designed to exhibit a high degree of specificity for the receptors found on the target plant cells. For instance, Su-Ji Joen et al. (2023) devised sucrose-coated nanocarriers aimed at targeting sugar membrane transporters in phloem cells to enhance the uptake of nanoparticles.²⁴² This level of precision ensures that the nanofertilizer interacts exclusively with the cells that require the supplied nutrient, dramatically reducing inefficiencies in delivery and utilization. In addition to targeting ligands, there are possibilities for surface modification of NMOFs with plant essential lipids, carbohydrates, protein domains, and peptides. These modifications can mimic the binding sites of natural ligands, facilitating the uptake of nutrients. This not only enhances plant growth and productivity but also contributes to efficient resource utilization, making it an exciting avenue in the field of nanofertilizer development.

Cost Implications of NMOFs

The cost implications of nanometal oxide fertilizers (NMOFs) must be carefully evaluated, as their use by growers will heavily depend on how they compare with conventional micronutrient fertilizers (**Table 4**).^{246,247} While comprehensive cost-benefit analyses of nanofertilizers are still limited, early studies suggest that the benefits of NMOFs may

outweigh the costs under specific conditions. Nanofertilizers such as ZnO-NPs and Fe₂O₃-NPs have demonstrated improvements in crop yields by 10-30% compared to traditional fertilizers, offering substantial economic benefits.²⁴⁶ This improvement in yield, when combined with the potential for reduced application rates, could lead to a significant increase in net revenue. For example, the application of ZnO-NPs increased net revenue from \$38.6 to \$103.1 per hectare compared to conventional ZnO fertilizers.²⁴⁸ One major factor influencing the cost-effectiveness of NMOFs is their nanoparticle properties such as size, surface area, and bioavailability. Smaller nanoparticles tend to have a higher surface area-to-volume ratio, which enhances nutrient solubility, uptake, and efficiency in plants. This allows for lower dosages compared to bulk micronutrient fertilizers, reducing overall material use and application costs despite the higher initial price of nanofertilizers. For instance, ZnO-NPs and CuO-NPs require application rates of 0.1-0.15 kg/ha, compared to conventional micronutrient fertilizers, which often require rates of 3-5 kg/ha. As a result, the cost per application for ZnO-NPs, at \$5.00 per hectare, is significantly lower than the \$25.00 per hectare cost for conventional zinc fertilizers.

Despite their higher initial costs, the enhanced efficiency of NMOFs can offset these expenses.²⁴⁶ This is attributed to the increased uptake efficiency of nanoparticles due to their small size and ability to penetrate plant cells more effectively than traditional fertilizers. This efficiency also aligns with environmental benefits, as fewer materials are applied to the soil, reducing the potential for runoff and environmental contamination. Furthermore, as synthesis techniques and scaling-up processes are optimized, the production costs of nanofertilizers are expected to decrease, making them more accessible and economically viable for widespread use. However, the variation in properties between different nanoparticles, such as composition, shape, surface charge, and solubility, plays a critical role in their behavior, cost, and effectiveness. For instance, nanoparticles with higher solubility, like ZnO-NPs, may

dissolve more quickly and be taken up by plants faster, while those with lower solubility, like TiO₂-NPs, may offer more controlled, long-term release. These variations can significantly impact both application rates and costs per hectare. Understanding these property-based variations is crucial for growers when selecting the appropriate nanofertilizer for specific crops and environmental conditions. Additionally, co-dosing strategies, where nanofertilizers are combined with conventional fertilizers, are being explored to optimize both cost and performance. This approach may help balance the benefits of enhanced nutrient delivery from nanofertilizers with the affordability of traditional fertilizers, reducing the overall cost and minimizing the risk of nanoparticle accumulation in food crops.

While the initial investment in NMOFs is higher, the long-term economic benefits through improved crop yields, particularly under conditions of biotic and abiotic stress, could be substantial. Nevertheless, concerns over potential environmental and safety risks associated with NMOF use could affect long-term costs, including regulatory compliance and the need for monitoring and management of their effects on soil health and ecosystems.

Table 4. Cost Analysis of Nanomaterial-Based and Regular Micronutrient Fertilizers; Data collected based on sources from scientific literature, industry reports, patent databases, and government and institutional reports.^{249–252}

Type of material	Cost per kg (USD)	Average Application Rate (kg/ha)	Cost per Application (USD/ha)
ZnO-NP	50	0.1	5.00
CuO-NPs	70	0.15	10.50
FeO-NPs	45	0.1	4.50
MgO-NPs	60	0.2	12.00
MnO-NPs	65	0.15	9.75
NiO-NPs	75	0.1	7.50
CaO-NPs	40	0.2	8.00
TiO ₂ -NPs	85	0.05	4.25
CeO-NPs	90	0.05	4.50
SiO ₂ -NPs	55	0.1	5.50
Regular Micronutrient Fertilizer (Zn)	5	5.0	25.00
Micronutrient Fertilizer (Cu)	10	3.0	30.00
Micronutrient Fertilizer (Fe)	8	4.0	32.00

Challenges

While NMOFs hold immense promise for revolutionizing agriculture, navigating the path to widespread adoption requires addressing several key challenges. One pressing concern is their potential impact on the intricate life within the soil. NMOFs' tiny size allows them to interact with plants and microbes in unprecedented ways, making it essential to understand these interactions fully. Researchers can study this through various scientific approaches. Laboratory experiments, including controlled environment tests and soil microcosms, can observe interactions between NMOFs and soil organisms like bacteria, fungi, and earthworms. Dose-response studies can determine the effects of different concentrations of

NMOFs on soil health and plant growth. Field studies, including pilot field trials and longitudinal studies, help monitor the real-world and long-term impacts of NMOFs on crops and soil ecosystems. Analytical techniques such as atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICP-MS), electron microscopy, and molecular biology methods like DNA sequencing and metagenomics can be used to measure and visualize NMOF concentrations and their effects on soil microbial communities. Ecotoxicological assessments, including toxicity tests and bioaccumulation studies, can determine potential harmful effects and the accumulation of NMOFs in soil organisms and plants. Computational modeling and simulation, including environmental fate models and risk assessment models, can predict the behavior and risks of NMOFs in soil and water systems. Interdisciplinary research involving soil scientists, ecologists, toxicologists, and agronomists, along with stakeholder involvement from farmers, policymakers, and industry, ensures comprehensive studies and practical applications. Developing standards, protocols, and regulatory frameworks based on robust scientific evidence is crucial for the safe use of NMOFs in agriculture. By employing these methods, researchers can ensure that NMOFs are used safely and effectively, balancing their benefits with potential environmental impacts.

Ensuring the safety of both farmers and consumers is paramount. Developing robust regulations and guidelines is essential to minimize potential human health risks associated with nanoparticle exposure. Nanoparticles can be inhaled, ingested, or come into contact with the skin, potentially leading to adverse health effects. Therefore, clear safety standards need to be established for the handling, application, and disposal of NMOFs. These regulations would include guidelines for safe exposure levels, proper protective equipment for those handling NMOFs, and protocols for safe application in the fields to prevent unintended exposure. Furthermore, these guidelines would address the safe integration of NMOFs into the food production process, ensuring that any residue on crops is within safe limits for

human consumption. This comprehensive regulatory framework would help protect the health of farmers applying these fertilizers and consumers eating the food produced using them.

While NMOFs boast enhanced nutrient delivery, their initial cost can be a significant hurdle for farmers accustomed to traditional fertilizers. This higher cost may deter farmers from adopting NMOFs despite their benefits. To make NMOFs economically attractive, it is crucial to conduct cost-benefit analyses. These analyses will compare the long-term benefits of using NMOFs, such as improved crop yields and reduced environmental impact, against their initial costs. Optimizing production processes can help lower the manufacturing costs of NMOFs. By improving the efficiency of production methods and scaling up manufacturing, the overall cost of NMOFs can be reduced, making them more affordable for farmers. This approach will help bridge the gap between the cost of traditional fertilizers and the potentially higher initial cost of NMOFs, encouraging wider adoption of this innovative technology.

Scaling up production to meet agricultural demands presents another challenge. Currently, producing NMOFs in large quantities remains a significant hurdle. Ensuring consistent quality and efficacy across diverse environmental conditions and a wide range of crops is essential for their success. For instance, it is crucial to determine whether these nanoscale fertilizers can perform consistently under the scorching sun in arid regions or the heavy rains of monsoon climates. Addressing these challenges is vital for NMOFs to fulfil their potential as a game-changer in sustainable agriculture. By optimizing large-scale production methods and rigorously testing NMOFs under various environmental conditions, we can unlock the true power of nanotechnology to nourish crops, protect our environment, and ultimately feed the world.

Future Perspectives and Research Directions

Progress in nanofertilizers and their responsible application in agriculture spans several crucial domains. First, it is important to explore the capabilities of hybrid and multi nutrient nanofertilizers across various applications and formulations. Customizing nanofertilizer blends tailored to specific crops and environmental conditions holds significant potential, including the possibility of generating climate-resilient strategies. Also, there's a need for continued research to advance controlled-release mechanisms and optimize fertilizer formulations for specific crops and soil types. However, because plants respond to nutrients only when they are limiting in the soil or plant, nutrient customization must be preceded by a comprehensive soil and plant testing regime to determine which nutrients are deficient.²⁵³ Nanoparticles provide an opportunity for precision in agriculture by enabling targeting of specific plant tissues or organs, ensuring precise nutrient delivery where it's needed most. In addition, ongoing exploration of nanoparticles for delivering essential elements and triggering plant defense mechanisms is also essential. These efforts will enhance the efficiency and sustainability of agricultural practices.

As captured by Vaidya et al. (2024),²⁵⁴ to fully understand the potential of NMOFs, it is essential to conduct comprehensive field studies to gain insights into their real life applicability and mechanisms for improving plant health and crop yields under the most environmentally relevant conditions. Exploring the synergistic effects of combining NMOFs with traditional fertilizers holds significant promise. Safety and sustainability considerations are paramount, necessitating the evaluation of the long-term impacts of nanofertilizer use on soil health and microbial community structure. The development of guidelines and best practices is critical for the safe and efficient application of NMOFs in agriculture. Understanding the environmental fate of NMOFs, including their interactions with various ecosystems, is an ongoing effort. The development of biodegradable NMOF formulations can address concerns related to environmental persistence and residue accumulation. Prioritizing

strategies to minimize potential health risks, particularly regarding toxicity or bioaccumulation, is imperative. Implementing rigorous environmental monitoring and establishing regulatory frameworks for responsible nanofertilizer usage and disposal is essential. Lastly, informed decision-making in nanofertilizer research necessitates interdisciplinary collaboration among experts in agronomy, environmental science, material science, plant biology, and nanotechnology. This interdisciplinary approach is indispensable for addressing the multifaceted challenges associated with nanofertilizers. Collaborative efforts among growers, researchers, policymakers, and industry stakeholders are pivotal to ensure the sustainable development and utilization of nanofertilizer technologies. Embracing these future perspectives and research directions will enable us to fully harness the potential of nanofertilizers while safeguarding agricultural productivity and environmental well-being.

Conclusion

Nano-sized metal oxide fertilizers represent a promising advancement in sustainable agriculture, offering the potential to enhance crop resilience, nutrient efficiency, and soil health. By leveraging their unique properties for controlled nutrient release and targeted delivery, NMOFs can address critical issues such as micronutrient deficiencies and environmental degradation associated with traditional fertilizers. However, realizing the full potential of NMOFs requires addressing challenges related to toxicity, regulatory compliance, cost, and scalability. It is also crucial to ensure that these innovations do not disrupt existing agricultural practices but rather integrate seamlessly to support farmers in their efforts to maintain productivity and sustainability. Continued interdisciplinary research and collaboration among scientists, policymakers, and industry stakeholders are essential to optimize the safe and effective use of NMOFs in agriculture, ultimately contributing to global food security and environmental sustainability.

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Conflict of Interest

The authors declare no conflict of interest.

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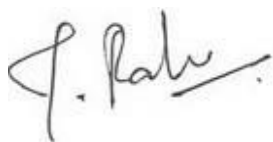
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No primary research results, software, or code have been included, and no new data were generated or analyzed as part of this review. All data supporting the findings of this study are derived from previously published sources, which have been appropriately cited in the reference section of this article.



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Behalf of all authors

Sincerely,

Raja muthuramalingam